ABSTRACT OF THESIS

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Degree Doctor of Philosophy. *Date* May, 1963.

Title of Thesis Studies in the Dithiole Series.

Using previously developed methods, several new dithiolium salts have been prepared, and others have been synthesised by modification of known methods.

3-Benzyl-5-phenyl-I,2-dithiolium perchlorate has been prepared by reaction of benzoylphenylacetone with hydrogen disulphide in ethereal hydrogen chloride, 3-chloro-5-phenyl-I,2-dithiolium perchlorate by chlorination of 5-phenyl-I,2-dithiole-3-thione, and the unsubstituted I,2-dithiolium cation by peracetic acid oxidation of I,2-dithiole-3-thione.

Peracetic acid oxidation of I,3-dithiole-2-thione and its 4-phenyl derivative provided the I,3-dithiolium system and its 4-phenyl derivative. Cyclisation of S-phenacyl-phenyl (dithioacetate) in ether with boron trifluoride furnished the known 2-benzyl-4-phenyl-I,3-dithiolium cation.

The reactions of several dithiolium salts with nucleophilic reagents have been studied.

The I,2-dithiolium cation and its 4-phenyl derivative decomposed by reaction with anionic species to produce I,2-dithiole-3-thiones but the 4-phenyl compound produced 4-phenylisothiazole by reaction with ammonium acetate. Reaction in benzene suspension with ammonia produced bis (4-phenyl-I,2-dithiole-3-yl) sulphide. With aniline it produced cis-phenylmalondialdehydedianil.

Related reactions of 5-phenyl and 3,5-diphenyl-I,2-dithiolium perchlorate produced anilinopropenethione derivatives.

In cold ethanol methylaniline reacted with 5-phenyl-I,2-dithiolium perchlorate to produce one of the above types of derivatives. In hot ethanol a hydride ion was lost oxidatively to produce 3-(p-methylaminophenyl)-5-phenyl-I,2-dithiolium salt. A similar reaction with 4-phenyl-I,2-dithiolium perchlorate failed to give a solid product.

3,5-Diphenyl-I,2-dithiolium perchlorate reacted with sodium ethoxide to produce 3-ethoxy-3,5-diphenyl-I,2-dithiole. With diethyl-sodiomalonate it furnished 4,6-diphenyl-3-ethoxycarbonyl-thiopyran-2-one by rearrangement.

2,4,5-Triphenyl-I,3-dithiolium perchlorate reacted with ethoxide and cyanide ions to produce the corresponding 2- substituted triphenyl-I,3-dithiole derivatives. Ammonia gave the 2-amino derivative, but in alcohol or acetic acid this decomposed with the production of desoxybenzoin, thiobenzamide, triphenyl-I,3-dithiole and triphenyl thiazole.

Use other side if necessary.

3-Methyl-5-phenyl-I,2-dithiolium perchlorate condensed with itself and with 3,5-diphenyl-I,2-dithiolium perchlorate to produce 6-methyl- and 6-phenyl-4-phenyl-2-thiophenacylidenethiopyrans respectively.

In the presence of base, 3-methyl-I,2-dithiolium and 2-methyl-I,3-dithiolium salts condensed with methylthiodithiolium salts to produce monomethine cyanine dyes. Attempts to prepare the trimethine cyanines by their condensation with ethylorthoformate were only partially successful.

New methods of syntheses of "thiothiophthenes" have been developed. Thioacylation of 3-methyl-5-phenyl-I,2-dithiolium perchlorate with methyldithiobenzoate produced the diphenyl derivative. This was also formed by sulphurisation of the corresponding 3-phenacylidene-I,2-dithiole, prepared by reaction of 5-phenyl-I,2-dithiole-3-thione with diazoacetophenone, or by condensation of its methiodide with sodium benzoylacetate.

Some of the results obtained for this thesis have been published in a paper in Journal of the Chemical Society.

TO MY PARENTS AND TO ALISON.

ACKNOWLEDGEMENTS.

I would like to take this opportunity of expressing my gratitude to Dr. D. Leaver for his help and guidance supplied during this research.

I would also like to thank the University of Edinburgh for the provision of laboratory facilities, the Department of Scientific and Industrial Research for a maintenance allowance, and Dr.A . Rudowski for his help with a Russian paper.

Finally, I would like to express my gratitude to my fiancée, Miss A.F. Taylor, who typed this thesis with such great patience.

My apologies are due to members of the staff and to the students of the Chemistry Department for the inconvenience caused by a prolonged assault on their olefactory organs by various sulphur compounds.

D. M.M.

STUDIES IN THE DITHIOLE SERIES.

By

DAVID MACKIE McKINNON.

UNIVERSITY OF EDINBURGH.

JULY, 1963.

INDEX.

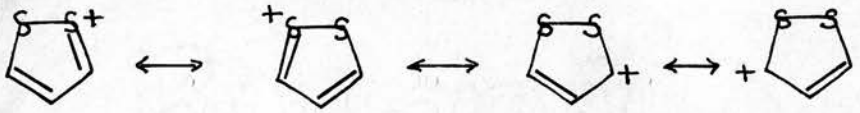
INTRODUCTION.

GENERAL.

When a sulphur atom replaces a -CH=CH- group in an aromatic ring, a new molecule is formed which is similar in many of its properties to the original one. Thus, by successive replacements, the tropylium cation(I) gives rise formally, first to the thiapyrylium cation(II), and then to the dithiolium cations, of which there are two isomeric forms, the I,2-dithiolium cation(III) and its I,3-isomer(IV).

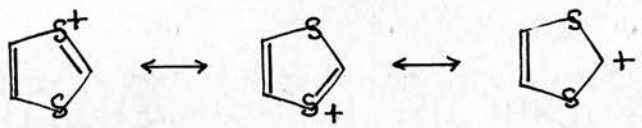
(I) (II) (III) (IV)

These dithiolium cations would accordingly have the following resonance structures.



(III)

a. b. c. d.



(IV)

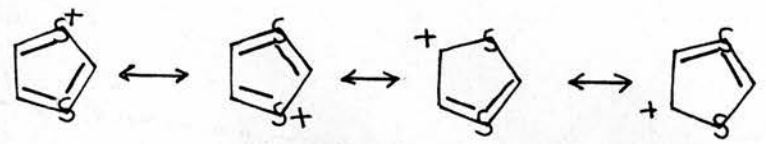
a. b. c.

Thus the I,2-dithiolium cation is a hybrid of two contributing sulphonium ions and two carbonium ions, and the I,3-cation of two sulphonium ions and one carbonium ion. On a qualitative basis this leads to the conclusion that the respective sites of nucleophilic attack should be position 3 in cation(III), and position 2 in cation(IV).

The use of 3d orbitals in the bonding of the sulphur atom, so that its outer shell may be expanded from eight to ten electrons, can also give rise to further canonical structures by regarding the replacement as one of =S= for =CH-CH=.

(III)

e. f. g.

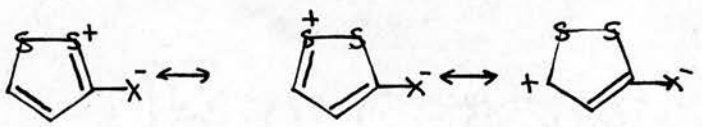


(IV)

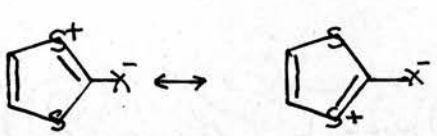
d. e. f. g.

Appreciable contributions of structures of these types might tend to facilitate nucleophilic attack at position 4 in both isomers.

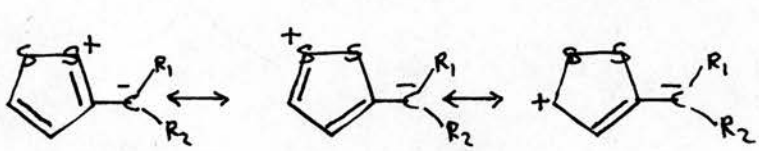
Potentially aromatic structures are those in which the five membered ring contains one double bond, while another double bond is exocyclic. Compounds containing this type of structure are dithiolones (V)(VI), dithiolethiones (VII)(VIII), and the alkylidene dithioles(IX)(X). These may give rise to charge-separated polar structures, with consequent resonance stabilisation involving the different canonical forms.



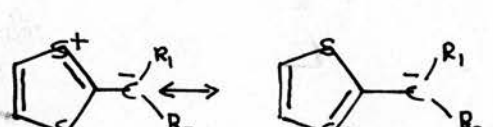
(V) X=O
(VII) X=S.



(VI) X=O
(VIII) X=S.



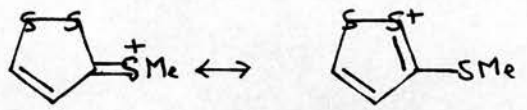
(IX)



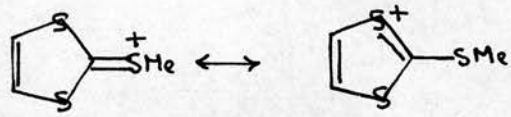
(X)

This resonance stabilisation would lead to reduction of the olefinic character in these compounds.

The methiodides of dithiolethiones(XI)(XII), may be considered as methylthiodithiolium salts with the following contributing structures.



(XI)



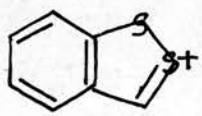
(XII)

In these, the activated ring structures are the same as in the corresponding unsubstituted dithiolium salts.

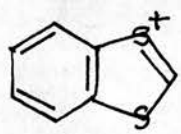
From the preceeding considerations, it would seem likely that the reactivity of these compounds should parallel that of the tropylium or thiapyrylium compounds, and that the system should be susceptible to nucleophilic, but not electrophilic attack. Electron attracting substituents should stabilise it by making possible an increase in the number of structures contributing to the resonance hybrid. On the basis of the resonance theory, this will produce greater stability.

The 4,5-benzo-I,2-dithiolium(IIIb), 4,5-benzo-I,3-dithiolium (IVb), and I,3-dithiolium (IV) cations have been the subjects of examination by M.O.and L.C.A.O. methods.[I,2,3.] The radical, anion and cation derived from benzo-I,3-dithiole were examined for three different values (0·6,0·8,and I·0) of the parameter α, the ratio of the overlap integrals of the -S- and -CH=CH-. The Longuet-Higgins method,[4] which was used to define the electron orbitals of sulphur, involves the use of 3d orbitals. In each case the delocalisation energy of the cation was greater than that of the radical or anion. In all of these, it followed from the values of electron densities or free-valencies, and from atomic localisation energies that the reactivity of position 2 is very high compared with other positions.

The resonance energy of the unsubstituted I,3-cation fell off rapidly with decreasing values of the parameter α. The Berthier and Pullman model.[5] in which it is assumed that 3d orbitals of



(IIIb)



(IVb)

sulphur do not take part, indicated a greater probability for the existence of the cation than did the Longuet-Higgins model. The comparative delocalisation energies were, in k.c./mole.

Cation.	Pullman, Berthier.	Longuet-Higgins.			
		α	0·6	0·8	I·0
I,3-unsubstituted	60		25	43	-
Benzo-I,3.	89·5		62	77	

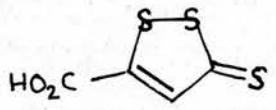
A further study[3] indicated the reactive positions of the I,2 and I,3-dithiolium cations from results based on the Longuet-Higgins model.

	Positions.	
Type of Reaction.	I,2-cation.	I,3-cation.
Nucleophilic	3	2
Free Radical	3	2
Electrophilic	4	4

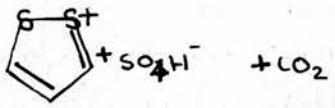
However, electrophilic substitution was considered unlikely. The bonds of maximum order were found to be between 4 and 5 positions for the I,2-dithiolium cation and between the 3 and 4 positions for the I,3-dithiolium cation.

Preparations of I,2-Dithiolium Salts.

Oxidation of I,2-dithiole-3-thiones in acetone solution with 3 equivalents of peracetic acid produces the corresponding dithiolium salt, in which a hydrogen atom replaces the thione group, eliminated as the hydrogen sulphate anion.[6,7]. This method, analegous to the preparation of thiazoles and imidazoles from their mercapto derivatives,[8,9,10] has been used to prepare the unsubstituted I,2-dithiolium cation from 5-thio-I,2-dithiole-3-carboxylic acid, (XIII), by spontaneous loss of carbon dioxide.

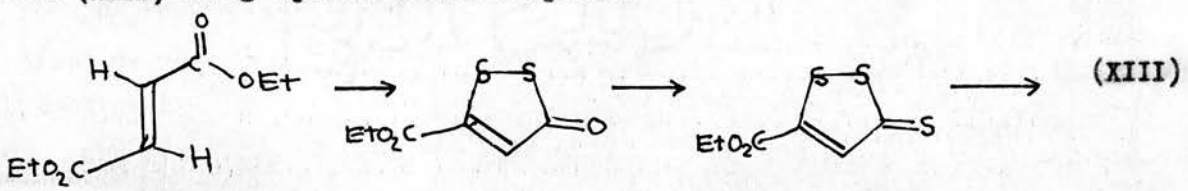


(XIII)



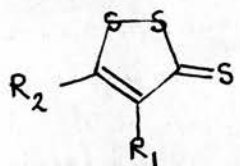
(III).

The acid was prepared from diethyl fumarate (XIV) by boiling with sulphur, to produce the ester (XV), sulphurisation to the thione (XVI), using phosphorus pentasulphide, and subsequent hydrolysis to the acid (XIII) using aqueous sodium sulphide.[6].

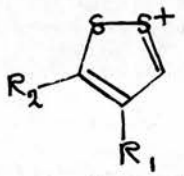


(XIV) (XV) (XVI) (XIII)

By similar methods, the 3-phenyl (XVIIIa) and 4-phenyl (XVIIIb) cations were produced[7] from 5-phenyl- (XVIIa), and 4-phenyl-I,2-dithiole-3-thione (XVIIb) respectively.



(XVII) a R_1=H, R_2=Ph.
b R_1=Ph R_2=H.

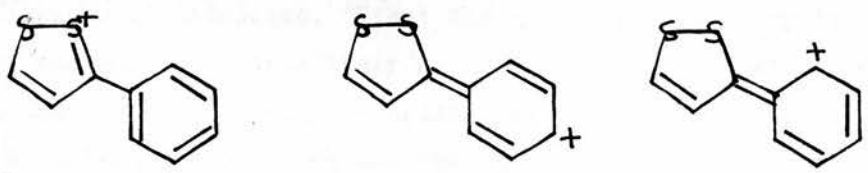


(XVIII) a R_1=H, R_2=Ph
b R_1=Ph, R_2=H.

Ultra-violet and nuclear magnetic resonance spectroscopic investigations have been made. N.M.R. indicates the symmetry of the 4-phenyl compound; the hydrogen atoms attached to the hetero-ring are represented by a

single peak, at 2/5 the intensity of the peak due to the phenyl protons, showing the equivalence of the two protons in the 3- and 5- positions. In the case of the asymmetrical 3-phenyl compound, the protons on the hetero-ring are represented by two doublets, showing their non-equivalence.

The ultra-violet spectra of the phenyl compounds are explicable in terms of resonance theory; whereas the 3-phenyl group may accept some of the positive charge in the contributing canonical forms (XIX,a-c),

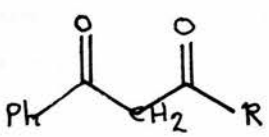


(XIX) a b c

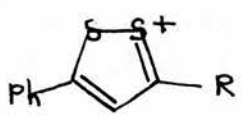
the 4-phenyl group is incapable of this. Hence the 3-phenyl group exerts a stronger bathochromic effect ($\lambda max.$=356mμ) than the 4-phenyl group (λmax=242mμ).

These hydrogen sulphate salts are soluble in water. Addition of the respective anion precipitates the insoluble perchlorates,iodides, bromides or thiosulphates.

Hydrogen disulphide condenses with I,3 diketones to give 3,5-disubstituted I,2-dithiolium salts in benzene solution saturated with hydrogen chloride.[II]. Thus 3,5-diphenyl (XXIa) and 3-methyl-5-phenyl-I,2-dithiolium[XXI] salts were produced from dibenzoyl methane (XXa) and benzoyl acetone (XXb) respectively.



(XX) a R=Ph
b R=Me

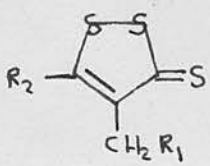


(XXI) a R=Ph
b R=Me

Acetylacetone under the same conditions produced an uncrystallisable oil which was insoluble in benzene.[IIb]. The salts, precipitated as the chlorides, were converted to the more stable perchlorates.

With these compounds, interannular conjugation between the phenyl groups and the dithiole ring is possible. Hence, as above, a bathochromic shift is expected. In these cases, a strong absorption is found in the region 350 - 400 mμ.

Treatment of I,2-dithiole-3-thiones (XXII) in glacial acetic acid with gaseous chlorine produces compounds which have been formulated as 3,3-dichloro-I2-dithioles,[12] but their slight solubility in non-polar solvents, and relatively high solubility in polar solvents suggests that they are really 3-chloro-I,2-dithiolium chlorides. As will be seen later, one of the chlorine atoms may be readily replaced by perchlorate ion, suggesting that ionic and not covalent bonding is involved. Partial chlorination produces compounds with a sulphur: chlorine ratio of 3:I, tentatively identified as monochlorine adduct.



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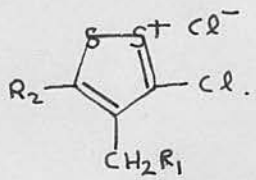


(XXIII)

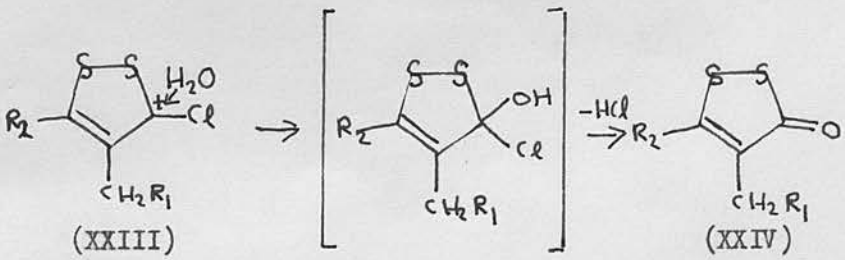
a R_1=H, R_2=H

b R_1=tBu, R_2=H

c R_1=H, R_2=tBu.

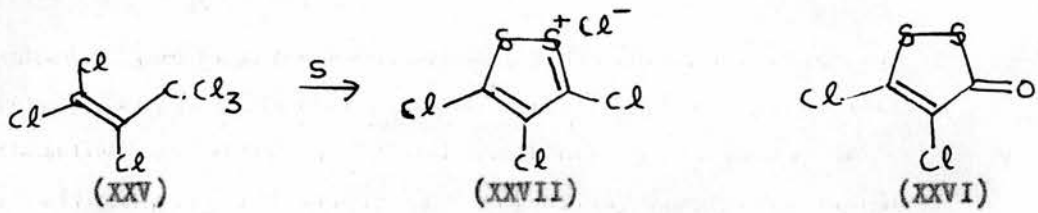
The compounds produced in this way were the 4-methyl, 4-neopentyl, and 4-methyl-5-t-butyl-3-chloro-I,2-dithiolium chlorides (XXIII a, b, c respectively)

Hydrolysis of the salts with dilute acetic acid produces the corresponding dithiolones (XXIV). This was taken as evidence for the attachment of both chlorine atoms to the same carbon atom, but the reaction may equally well be regarded as a nucleophilic displacement of chlorine from the cation.



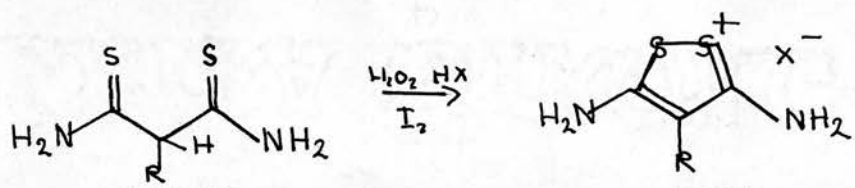
(XXIII) (XXIV)

The compound obtained by Boberg[13], by reaction of hexachloropropene (XXV) with sulphur is probably similarly constituted in view of its high melting point. With water it also is hydrolysed to a dithiolone (XXVI). It may be named 3,4,5-trichloro-1,2-dithiolium chloride. (XXVII)



(XXV) (XXVII) (XXVI)

Oxidative ring closure of dithiomalonamides produces 1,2-dithiolium salts.[14] Thus, substituted dithiomalonamides (XXVIII) in the presence of mineral acid give 4-substituted 3,5-diamino-1,2-dithiolium salts (XXIX) by oxidation with hydrogen peroxide. The use of iodine as the oxidizing agent produces the iodides.



(XXVIII) (XXIX)

R=H, $-CH_2.CH_2.CN$, C_6H_5.

The salts produced were those of the 3,5-diamino, and the 4-(β-cyanoethyl)- and 4-phenyl-3,5-diamino cations. The salts were pharmacologically and toxicologically tested for resemblances to the naturally occurring antibiotics Aureothricin, Holomycin, and Thiolutin, which are discussed below.

1,2-Dithiole-3-thiones, (XXX) prepared by treatment of suitable three-carbon compounds with phosphorus pentasulphide, sulphur, or a combination of these two reagents, yield the corresponding 3-methylthio-1,2-dithiolium salts (XXXI) when treated with the methyl esters of inorganic acids. In this connection, dimethyl sulphate and methyl iodide are almost invariably used.

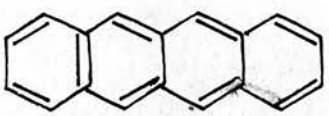
(XXX) (XXXI)

3-Alkylidene-I,2-Dithiole Derivatives.

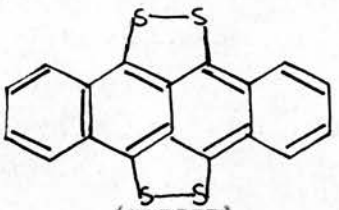
Compounds with a double bond exocyclic to the dithiole nucleus at position 3 can be converted to 3- substituted I,2-dithiolium cations by the addition of a proton. Thus they may be viewed as the anhydrobases of derivatives of 3-methyl-I,2-dithiolium salts.

Naphthacene-5,6:II,I2-Bis-Disulphides.

The action of sulphur[15] or sulphur monochloride[16] on naphthacene (XXXII) produces a green compound containing four atoms of sulphur, formulated as the 5,6:II,I2-bis-disulphide (XXXIII) which can also be regarded as the anhydrobase of a bis-I,2-dithiolium dication.



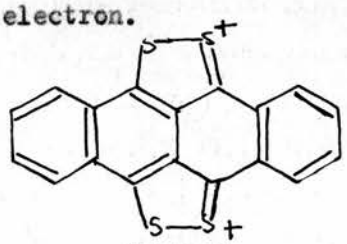
(XXXII)



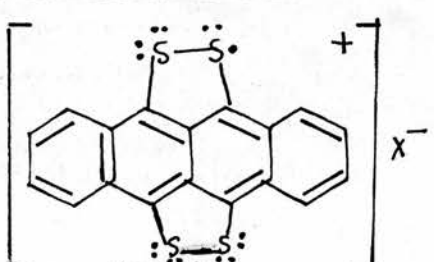
(XXXIII)

Thus it is possible that the addition of acid to this molecule might produce the bis-dithiolium salt. In practice,however, this is not found, and instead there are produced other salts, yellow in colour, derived by oxidation of the original compound. Thus, in oxidizing acids, compounds of formula $C_{18}H_8S_4^{2+}.2\,X^-$ were produced. The action of halogens gives similar products, bromide and chloride salts being obtained.

These salts are probably derived by oxidative loss of two electrons from the starting compound, to produce the dication.(XXXIV) The dication and the parent compound react together to produce a mono-cation (XXXV) of red colour. This is formulated with an unpaired electron.

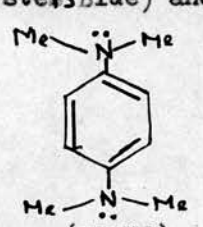


(XXXIV)

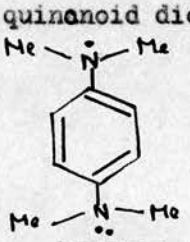


(XXXV)

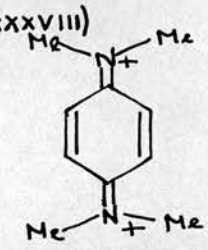
The monosalts are also formed by the oxidation of the bis-disulphide in dilute acids, when ½ an atom of oxygen is used per molecule. In the absence of air no reaction occurs. These oxidations belong to a general type of electron-transfer reaction of which the best known example is the oxidation of N,N,N',N'-tetra-methyl-P-phenylenediamine first to the radical cation (Wurster's Blue) and then to the quinonoid dication.[95]



(XXXVI)



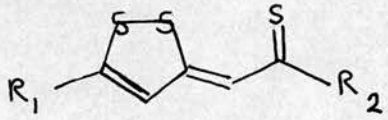
(XXXVII)



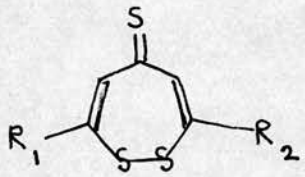
(XXXVIII)

Thiothiophthenes.

This is the name which has been given to compounds of the structure (XXXIX).



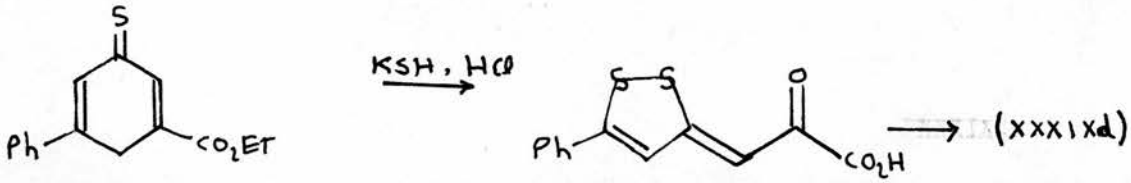
(XXXIX)



(XL)

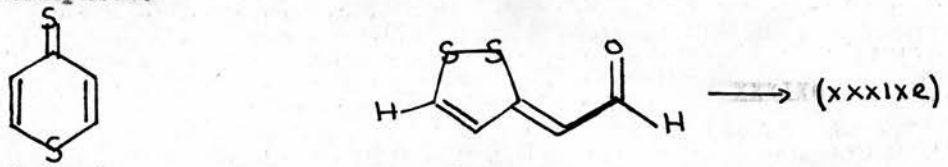
a R_1=CH_3, R_2=CH_3
b R_1=Ph, R_2=Ph
c R_1=Ph, R_2=CH_3
d R_1=Ph, R_2=H
e R_1=H, R_2=H.

The heating of diacetyl acetone with phosphorus pentasulphide in boiling benzene affords a compound which was originally formulated as a seven membered ring disulphide, (XL)[18] but which has now been shown to possess the structure (XXXIXa). Similarly, Traverso prepared the corresponding diphenyl (XXXIXb) and methyl-phenyl (XXXIXc) compounds[44] from dibenzoyl-acetone and acetyl-benzoyl-acetone respectively. The compound (XXXIXd) was prepared from 2-carbethoxy-6-phenyl-pyran-4-thione (XLI) by treatment with potassium-hydrogen sulphide, to form the acid (XLII), followed by treatment with phosphorus pentasulphide.



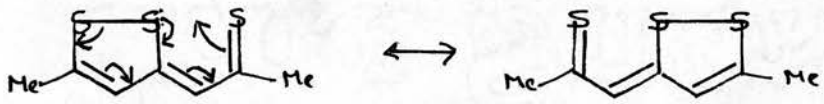
(XLI) (XLII)

The unsubstituted compound (XXXIXe) was prepared[33] from dithia-γ-pyrone (XLIII) by treatment with mercuric chloride, to form the intermediate ketone (XLIVa), followed by treatment with phosphorus pentasulphide.

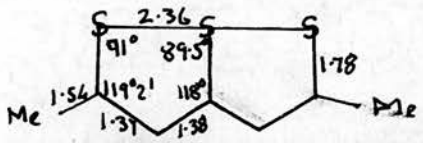


(XLIII) (XLIVa)

An X-ray investigation indicated the structure (XXXIXa).[19] Bond lengths and angles were given. The sulphur atoms were found to be collinear. The molecule was symmetrical owing to "no-bond resonance", i.e. it is a resonance hybrid of two canonical forms.



XXXIXa



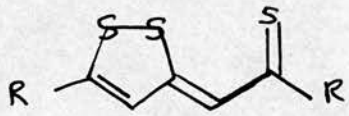
It is worth noting that the S-S bond length in disulphides is 2·04A. Thus in this compound the bond order is less than unity.

It has been suggested[20] that these results can be better explained by the delocalisation of all π electrons to form an 8-centered system (five carbon atoms and three sulphur atoms). The S-S bonds are described as being purely π bonds, without any σ bonding, similar to the structure of the N-N bond in N_2O_4.[21] In the latter compound the bond distance is I·7A compared to that of the N-N bond in hydrazine which is I·48A. In each case there is a I5-I6% increase in bond length. This explains the difficulty of formation of the analogue with three

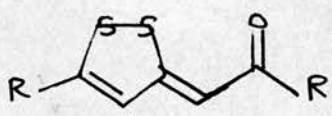
oxygen atoms, since the overlap integral of the oxygen p-orbitals is I/20th. that of the sulphur orbitals. In addition, it agrees with known bond length and angles.

Treatment of the trithio-compound with acid replaces one of the sulphur atoms with oxygen. The reverse process is effected by treatment of the ketone with phosphorus pentasulphide.[22,33].

The parent compound (XXXIXe) and its dimethyl derivative (XXXIXa) have been compared with the corresponding ketones (XLIV) by means of nuclear magnetic resonance.[22]



(XXXIX) e R=H
a R=CH_3



(XLIV) a R=H
b R=CH_3

The spectrum of (XXXIXa) consisted of two lines, one of which was assigned to the CH_3 protons, and the other to the methine protons. This is what would have been expected of an entirely symmetrical structure, with two equivalent protons of one type and six of another.

The spectrum of the keto-compound (XLIVb) showed four structurally different proton groups, which eliminated the possibility of the dithiepin type of structure (XL) originally postulated.[18] The lines could be assigned entirely to the structure (XLIV), to the two different types of methyl protons, and to the two different methine protons.

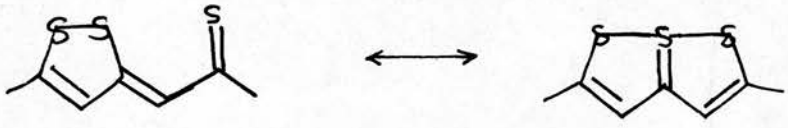
The spectrum of the compound (XXXIXe) showed two doublet lines. These were typical of spin-spin interaction. One of these was assigned to the equivalent protons at each end of the molecule, while the other was assigned to the remaining pair of equivalent methine protons.

The spectrum of the compound (XLIVa) was more complicated. It showed four doublets, each of which corresponded to one of the protons in the structure given.

The carbonyl groups in the ketones (XLIVa) and (XLIVb) have normal properties since they give 2,4-dinitrophenyl-hydrazones quite easily. On the other hand, compound (XXXIXe,a) was not reactive under the same conditions. This showed that in this case the thio-carbonyl group no longer existed as such, but was completely merged into the bicyclic mesomeric "no-bond resonance" system.

A new nomenclature for these compounds has been proposed, in conjunction with the Beilstein Institute. Thus the parent compound (XXXIXe) would be named; meribicyclo-I,3-epidithio-pentadiene-5-thial. The parent dithiole-ketone (XLIVa) is I,3-epidithio-pentadiene-5-al.

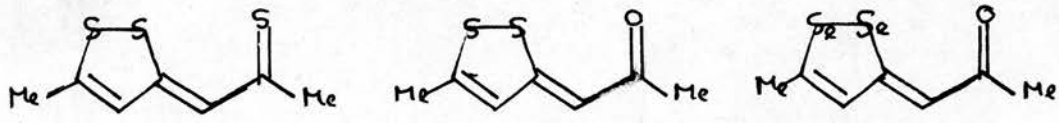
Maeda[23] has investigated the participation of the d-orbitals in the hybridisation of the sulphur atoms forming the linear S-S-S bond of thiothiophthene. This would involve the following canonical forms. (XLV).



(XLV)

The calculations showed that the participation of the 3Pz orbital was more likely than that of the 3dxy orbitals.

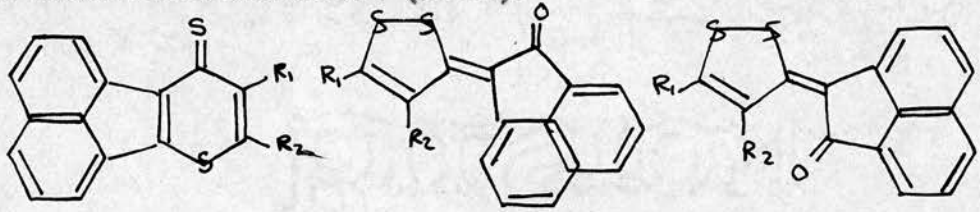
In a study[24] of the dipole moments of three related compounds, it was found that the increasing ketonic character postulated on this basis agreed with the tendency for formation of 2,4-dinitro-phenyl-hydrazones, which increased in the order compound (XXXIXa) < the ketone (XLIVb) < the ketone (XLVI).



(XXXIXa) (XLIVb) (XLVI)

A Raney-nickel desulphurisation on the compounds (XXXIXa and b) produced methyl-n-amyl ketone and δ-phenyl-butyl-methyl ketone respectively.[25].

Acenaphthenone Derivatives. Reaction of acenaphthenone with dithiolethiones in alcoholic potassium hydroxide, or with their methiodides in pyridine has produced dithiole derivatives of the above mentioned type. (XLVIII) When the dithiole nucleus was not substituted in position 5, condensation took place with rearrangement and reduction to give thiofluoranthenethiones. (XLVII).[26,27]

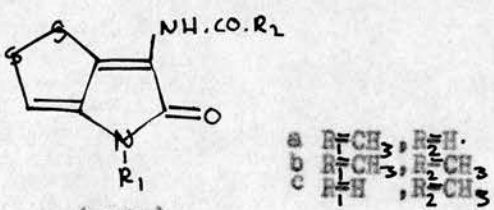


(XLVII) cis (XLVIII) trans

The ketones (XLVIII) could be converted into the corresponding thiones by means of phosphorus pentasulphide.

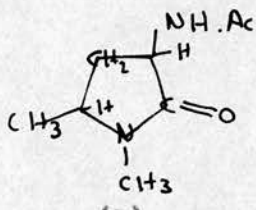
The carbonyl and disulphide groups in the compound (XLVIII) were assigned the "trans" configuration with respect to the interannular double bond on the basis of a comparison of the infra-red carbonyl absorptions with those of the compounds (XLIV). The carbonyl frequencies of compounds (XLVIII) were normal for those of α,β-unsaturated ketones, but the lower carbonyl frequencies found in compounds (XLIV) could only be accounted for by postulating some kind of interaction with the neighbouring sulphur atom of the dithiole ring.[26]

The Dithiole Antibiotics. From the fermentation broths of "Streptomyces" strains have been isolated three antibiotics[28,29] (XLIXa,b,c), all of which contain the 1,2-dithiole nucleus with an exocyclic double bond.



(XLIX)

a $R_1=CH_3$, $R_2=H$.
b $R_1=CH_3$, $R_2=CH_3$
c $R_1=H$, $R_2=CH_3$

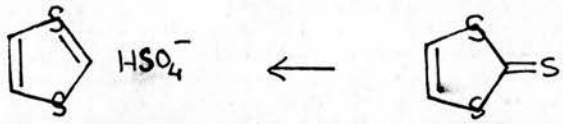


(L)

These structures have been elucidated by the hydrolysis and Raney-nickel desulphurisation of thiolutin to "desthiolutin" (L) which has been synthesised unambiguously.

I,3-Dithiolium Salts.

The I,3-dithiolium salts (LI) may be obtained from I,3-dithiole-2-thiones (LII) by peracetic acid oxidation in acetone solution.[30]



(LI) (LII)

α-Oxo-alkyl-dithiocarboxylates (LIII), prepared by the reaction of α-halo-ketones with the sodium salts of dithiocarboxylic acids, are cyclised in anhydrous ether saturated with hydrogen chloride to yield I,3-dithiolium chlorides. (LIV)[II]

(LIII) (LIV)

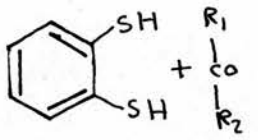
a R_1=Ph, R_2=Ph, R_3=H.

b R_1=Me, R_2=Ph, R_3=H.

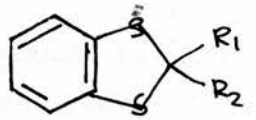
c R_1=Ph, R_2=Me, R_3=H.

When hydrogen sulphide is used in the cyclisation as well as hydrogen chloride, yields are improved and reaction times diminished. The use of boron trifluoride in place of hydrogen chloride in the cyclisation of phenacyl-dithioacetate (LIIIb) produces a better yield of salt. α-Phenyl-phenacyl-dithiobenzoate (LIII, R_1=R_2=R_3=Ph.) fails to cyclise under the usual conditions, but triphenyl-I,3-dithiolium-perchlorate (LIV, R_1=R_2=R_3=Ph.) is obtained in good yield when the cyclisation is carried out in boiling acetic acid containing perchloric acid under a stream of hydrogen sulphide.

Benzo-I,3-Dithiolium Salts. Benzene-I,2-dithiol (LV) reacts with suitable carbonyl compounds[31,32] to produce benzo-I,3-dithiole derivatives. (LVI)



(LV)



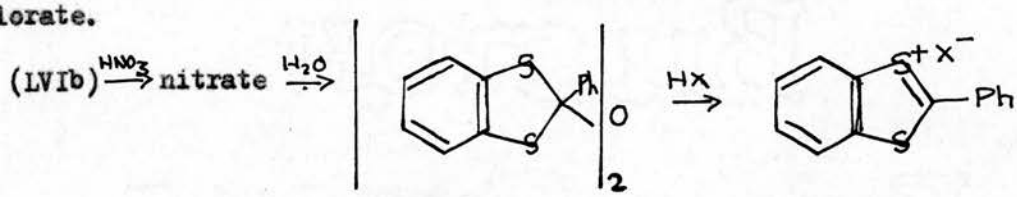
(LVI)

a R_1=Ph, R_2=Me

b R_1=Ph, R_2=H

c R_1=-CH=CH-Ph, R_2=H.

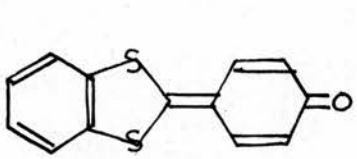
The compound (LVIb) is oxidised with nitric acid to form a complex mixture of nitrates. Hydrolysis of this yields an oxide (LVII) which on treatment with acid produces the 2-phenyl-4,5-benzo-1,3-dithiolium salts (LVIII) of the corresponding acid.i.e. nitrate, chloride and perchlorate.



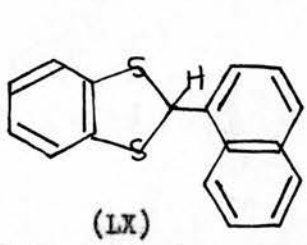
(LVII) (LVIII)

Cinnamaldehyde (LVc) similarly condenses to form the compound (LVIc) which can be oxidized to form the nitrate, but the base obtained by treatment with alkali was too unstable to be isolated.

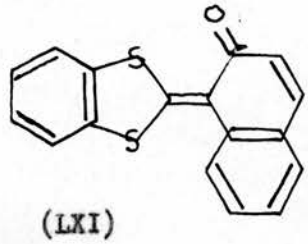
Substituents in the phenyl group may have hindering or helping effects on the oxidation[32]. Thus a 2-(O-nitro-phenyl) compound was produced, but it is unattacked by cold nitric acid, and boiling destroyed it. However, 2-(p-methoxy-phenyl) and 2-(p-hydroxy-phenyl) compounds are oxidised easily to nitrates. The former produces the oxide on basification, and hence the other salts, but the latter on basification loses the elements of water to produce the anhydrobase (LIX). A similar compound (LXI) is produced with the 2-(2-hydroxy-I-naphthyl)-derivative. Oxidation of this naphthyl derivative (LX) takes place so readily that it is impossible to isolate the hydroxy compound.



(LIX)



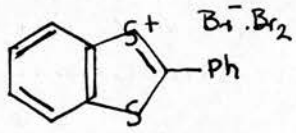
(LX)



(LXI)

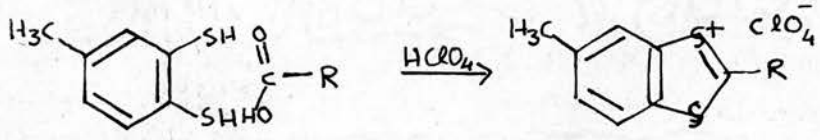
Instead, the condensation of I-formyl-2-hydroxy-naphthalene with benzene-I-2-dithiol in the presence of dilute acid produces the anhydrobase (LXI). From these anhydrobases the salts are regenerated on the addition of acid.

Reaction of the parent benzo-2-phenyl-I,3-dithiole with bromine produces a perbromide, formulated as the compound (LXII).



(LXII)

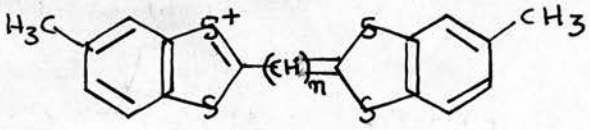
Starting from the related toluene-3,4-dithiol (LXIII) several I,3-dithiolium salts (LXIV) have been prepared[34] by condensation in the presence of perchloric acid, with acids, or acid chlorides.



(LXIII) (LXIV)

R=H,CH_3 R=H,CH_3

The reaction with malonic acid is interesting in that a further condensation takes place with loss of a proton to produce the monomethine cyanine (LXVa). Similarly, glutaconic acid produces the trimethine cyanine (LXVb).



(LXV)

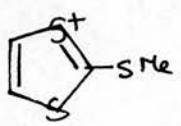
a n=I
b n=3.

2-Methylthio-I,3-dithiolium salts. As with I,2-dithiole-3-thiones, reaction of I,3-dithiole-2-thiones with the methyl esters of inorganic acids yields the 2-methylthio-I,3-dithiolium salt. Since the parent

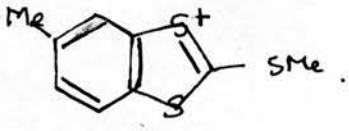
thiones are not so well known as in the I,2- series, examples of the salts are not so numerous in the literature.

The unsubstituted compound (LXVI) has been synthesised from the thione and methyl iodide in nitromethane.[35]

5-Methyl-2-methylthio-benzo-I,3-dithiolium hydrogen sulphate (LXVII) has been synthesised[36] from toluene-3,4-dithiol by reaction with carbon disulphide followed by dimethyl sulphate.

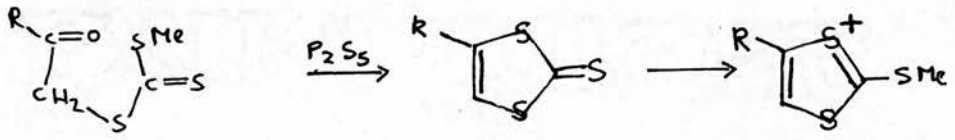


(LXVI)



(LXVII)

Acetonyl- and phenacyl- methyl-trithiocarbonates (LXVIII) are cyclised[IIb] by treatment with phosphorus pentasulphide in boiling tetralin to form the corresponding thiones. These on treatment with methyl iodide or dimethyl sulphate yield 4-methyl-and 4-phenyl-2-methylthio-I,3-dithiolium salts.(LXIX)



(LXVIII)

a R=Me

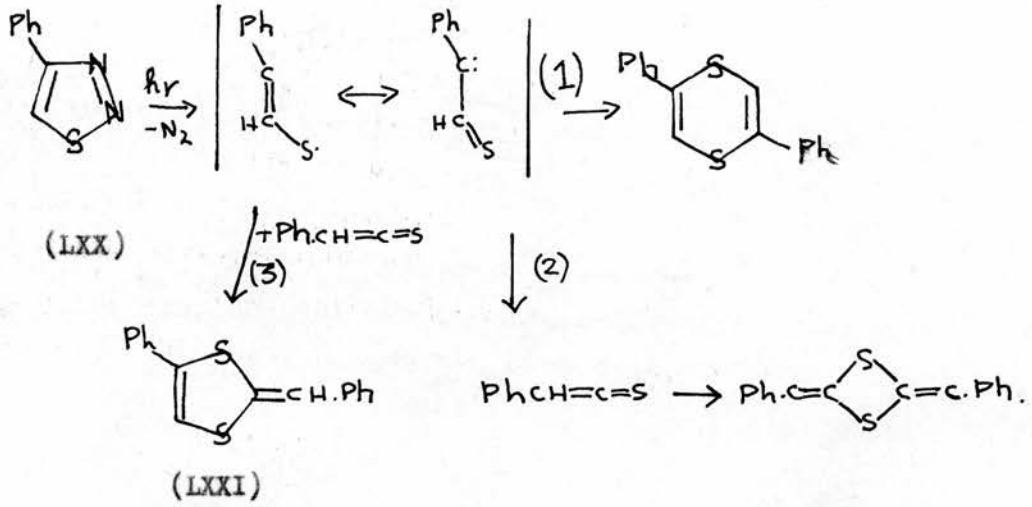
b R=Ph.

(LXIX)

a R=Me

b R=Ph.

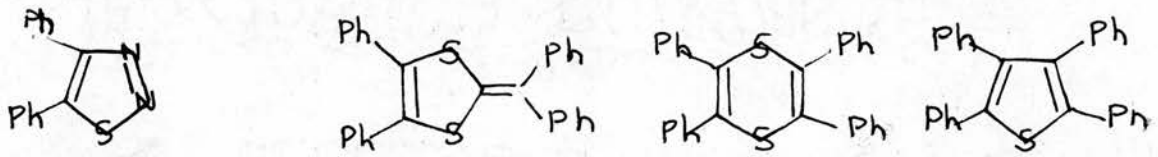
2-Alkylidene-I,3-dithiole derivatives. Such compounds are formed by the photolysis of I,2,3-thiadiazoles.[37] Their structures have been proved by Raney nickel desulphurisations, oxidation to disulphones, and by alkaline fission. The product of the photolysis of 4-phenyl-I,2,3-thiadiazole (LXX) was named 2, -diphenyl-I,4-dithia-fulvene.(LXXI) A better name is 2-benzylidene-4-phenyl-I,3-dithiole. The scheme postulated for the formation of the product from 4-phenyl-I,2,3-thiadiazole is shown below.



(LXX)

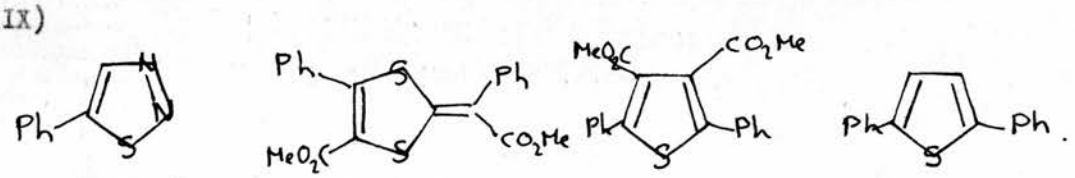
(LXXI)

In this scheme there are three possible products. In actual fact, mono-substituted thiadiazoles yield only dithiole derivatives. When the thiadiazole is disubstituted, reaction (I) becomes important, Thus tetraphenyl-dithiin (LXXIV) is produced as well as 2-benzhydrylidene-4,5-diphenyl-I,3-dithiole (LXXXIII) from 4,5-diphenyl-I,2,3-thiadiazole. (LXXII) The tetraphenyl-dithiin extrudes sulphur on heating to produce tetraphenyl-thiophen. (LXXV)



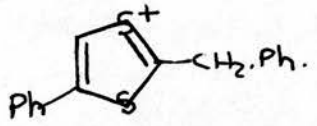
(LXXII) (LXXIII) (LXXIV) (LXXV)

Photolysis of 4-carbomethoxy-5-phenyl-I,2,3-thiadiazole (LXXV) produces the corresponding dithiole derivative (LXXVII) which in hydrolysis and decarboxylation yields the compound (LXXI). The other product of the reaction is 3,4-dicarbomethoxy-2,5-diphenyl-thiophen (LXXVIII) which probably arises from the original dithiin derivative by extrusion of sulphur. Hydrolysis and decarboxylation of this produces the known 2,5-diphenyl-thiophen. (LXXIX)



(LXXVI) (LXXVII) (LXXVIII) (LXXIX)

As expected of these dithiole derivatives, they are easily protonated in strong acid to produce I,3-dithiolium salts. Thus 2-benzylidene-4-phenyl-I,3-dithiole produces the 2-benzyl-4-phenyl-I,3-dithiolium cation (LXXX) by reaction with perchloric acid.



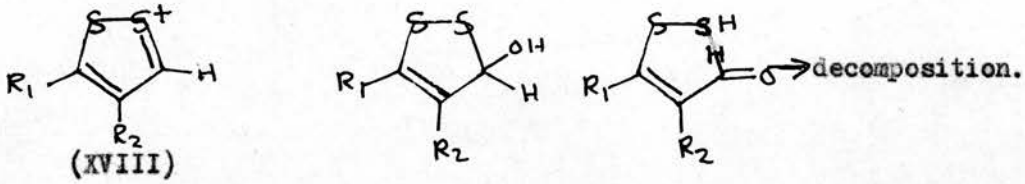
(LXXX)

The protonation of other derivatives of this type (LIX),(LXI) has already been described above.

Reactions of I,2-dithiolium salts.

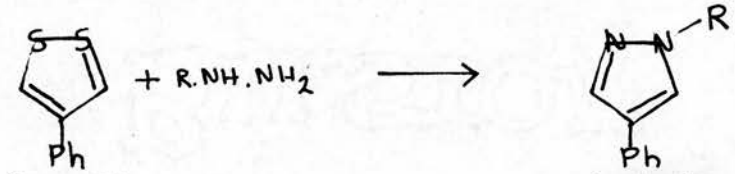
As explained above, dithiolium salts are expected to be reactive to nucleophilic, but not electrophilic reagents. Accordingly, in nitration, the dithiole ring is unattacked, and the 4-phenyl-I,2-dithiolium cation is nitrated in the p. position of the phenyl group, while the 3-phenyl-isomer is nitrated in the m- and p- positions.(7) This behaviour parallels the nitration of phenyl-pyrylium salts.(38,39)

Reaction of the dithiole ring with bases gives varied products. Thus, addition of hydroxide ion to a dithiolium salt causes decomposition,(7) with liberation of sulphur, presumably via the mechanism.



(XVIII)

A similar reaction has been observed with agueous hydrazine, but with 85% hydrazine hydrate, the 4-phenyl-I,2-dithiolium salt (XVIIIb) reacts to give a quantitative yield of 4-phenyl-pyrazole (LXXXIa)



(XVIIIb) (LXXXI)

a R=H

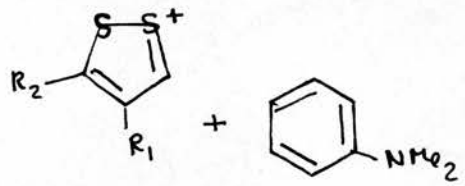
b R=Ph.

Monosubstituted hydrazines give similar results, with the formation of N-substituted pyrazoles. (LXXXIb)

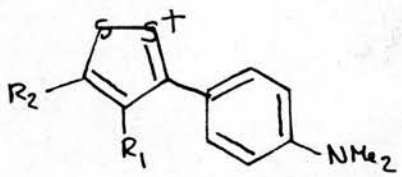
The use of N,N'-disubstituted hydrazines in the reaction produces N,N -disubstituted-pyrazolium salts(40) in 50-65% yield. This reaction predominates at temperatures below -2o C, but above this temperature, another reaction becomes important, namely, the sulphurisation of some of the dithiolium salt to produce the corresponding I,2-dithiole-3-thiones.

The sulphur required for this reaction arises by breakdown of some more of the dithiolium salt. The reaction is rapid in boiling pyridine, and with added sulphur, the yield of thione is quantitative even at room temperature.

In the reaction of these cations with tertiary aromatic amines, electrophilic attack by the cation on the p- position of the amine is followed by oxidative loss of hydride ion to give violet dyes[43](LXXXII) by way of a leuco intermediate. The parent dye (LXXXIIc) is produced by the peracetic acid oxidation of the corresponding 3(p-dimethylamino-phenyl) I,2-dithiole-3-thione.

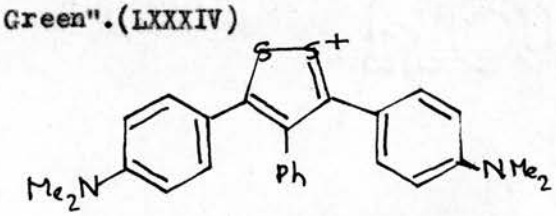


(XVIII)

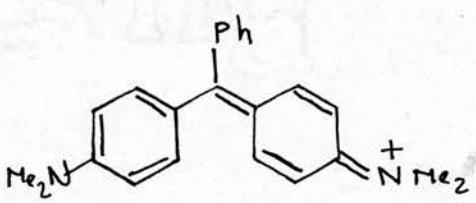


(LXXXII) a R_1=H, R_2=Ph
b R_1=Ph, R_2=H
c R_1=R_2=H.

In the case of the 4-phenyl compound (XVIIIb), further condensation occurs with another molecule of dimethyl aniline to produce the dithiolium counterpart (LXXXIII) of "Malachite Green".(LXXXIV)

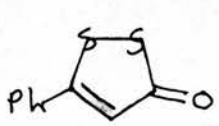


(LXXXIII)

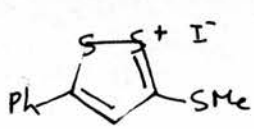


(LXXXIV)

The dyes (LXXXIIa) are also produced by condensation of dimethyl aniline with the dithiolone (LXXXV) in presence of phosphorus oxychloride, and with the thione methiodide.(LXXXVI)



(LXXXV)

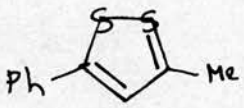


(LXXXVI)

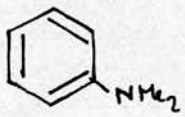
(LXXXVII)

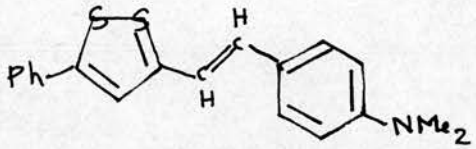
Reaction of 3,5-diphenyl-I,2-dithiolium perchlorate (XXIa) with dry ammonia in ethanol produces 3,5-diphenyl-isothiazole[II](LXXXVII).

A methyl group attached to the 3 position is reactive. Thus it may condense with aromatic aldehydes[II] to give styryl derivatives e.g. (LXXXVIII).



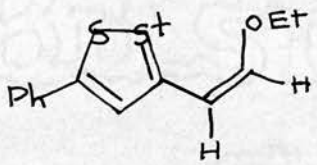
(XXIb)





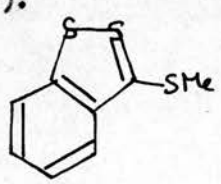
(LXXXVIII)

With triethyl-orthoformate, 3-(2- -ethoxyvinyl)-5-phenyl-I,2-dithiolium perchlorate[II](LXXXIX) is formed.

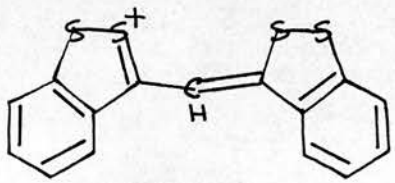


(LXXXIX)

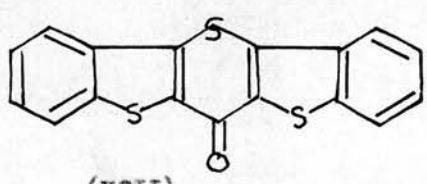
3-Methylthio-I,2-dithiolium salts may react in two ways. (a). by loss of methyl iodide to regenerate the thione, (e.g. with pyridine, the products are the thione and N-methyl-pyridinium iodide[27]). (b) by nucleophilic displacement of methanethiolate anion. Reactions of type(b) have already been described as forming the products (LXXXII),(XLVII) and (XLIII). Condensation of 4,5-benzo-3-methylthio-I,2-dithiolium iodide (XC) with malonic acid yields a product[41] which has been formulated as a cyanine (XCI). Reaction of the methiodide (XC) with acetone-dicarboxylic acid proceeds with loss of methyl mercaptan, carbon dioxide and hydrogen sulphide to produce bis-(2',3' thionaphtheno)-3,2:5,6-pyran-4-thione. (XCII).



(XC)

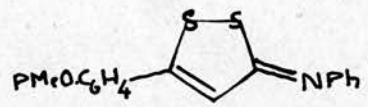


(XCI)

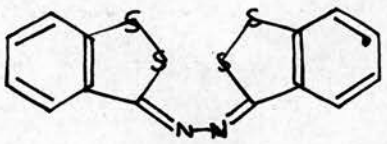


(XCII)

Primary aromatic amines react to give dithiole imines. Thus aniline reacts with 5-p-methoxyphenyl-3-methylthio-I,2-dithiolium iodide to produce the imine[42] (XCIII). Reaction of 4,5-benzo-3-methyl-thio-I,2-dithiolium iodide with hydrazine hydrate produces the azine[42] (XCIV).



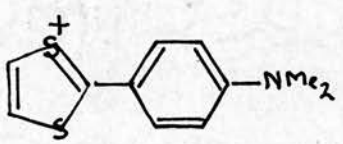
(XCIII)



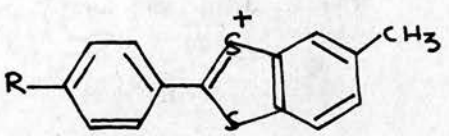
(XCIV)

Reactions of I,3-dithiolium salts.

These have reactivity similar to their I,2- isomers. The I,3-dithiolium cation condenses with dimethyl aniline [30] to produce a violet dye (XCV).

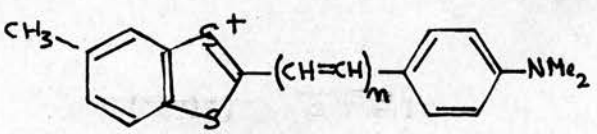


(XCV)



(XCVI) a R = OCH_3
b R = $N(CH_3)_2$

In the benzo-I,3-dithiolium series, a number of I,3-dithiolium dyes have been prepared by condensation with electron-rich aromatic compounds. Thus reaction with anisole and dimethyl-aniline produces derivatives of type (XCV). With p-dimethyl-amino-cinnamic acid, oxidation and decarboxylation produced the styryl compound [36] (XCVIIa).

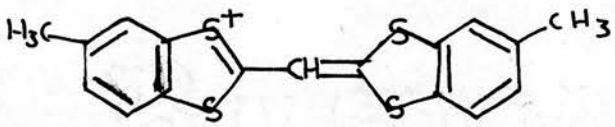


(XCVII) a n = 1
b n = 2

This same compound is produced by reaction of 2-methyl-benzo-I,3-dithiolium salts with p-dimethylamino-benzaldehyde; reaction with p-dimethylamino-cinnamaldehyde produces the vinylene homologue.(XCVIIb)

2-Methyl-4-phenyl-I,3-dithiolium perchlorate reacts with p-dimethylamino-benzaldehyde[II] to give a similar compound.

The 2-methylthio-benzo-I,3-dithiolium salts react with the p- position of anisole or dimethylaniline to produce dyes of type (XCIV). Their reaction with 2-methyl-I,2-dithiolium compounds produces a cyanine dye.[36](XCVIII).



(XCVIII).

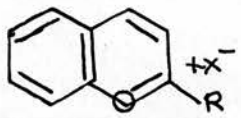
DISCUSSION.

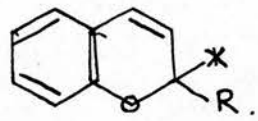
Object of Research.

In the present investigation, the main object was to study the reactions of dithiolium salts with nucleophilic reagents, and to compare these reactions with those of related cationic heterocycles such as pyrylium salts, thiapyrylium salts, and N-alkyl thiazolium salts. It was expected at the outset on consideration of these reactions, that any or all of the following types of reactions might be encountered.

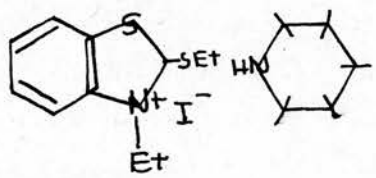
A). Nucleophilic attack on the nuclear carbon atom, without ring fission.

i). Without replacement of a substituent. This reaction occurs with benzopyrylium[45] and pyrylium salt[46]. The nucleophilic species adds on at a carbon atom. e.g.

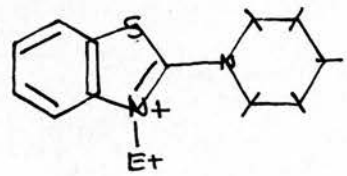




ii). With replacement by a substituent. Alkyl mercapto and halogen substituents on the nuclear carbon atom are eliminated. Thus, 3-ethyl-2(1-piperidyl)-4,5-benzothiazolium perchlorate (C c) is prepared by reaction of the 2-ethylthiothiazolium salt (XCIX) with piperidine[47].



(XCIX)



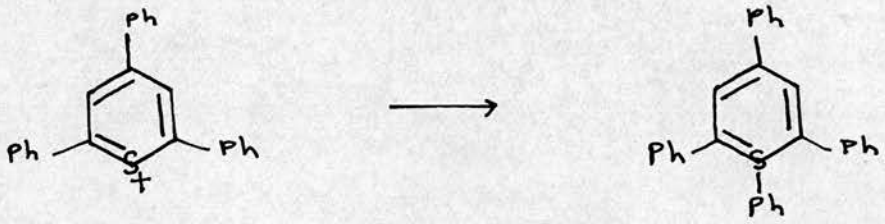
(C)

The reactions of dithiolium salts[30] and of benzodithiolium salts[36] with dimethyl aniline mentioned above are of this type. In these cases a hydride ion is lost oxidatively.

The reaction of 2-methylthiobenzodithiolium salts with 2-methylbenzodithiolium salt to give the cyanines[34] (XCVIII) is also included in this type. In this case, an alkylmercapto group is eliminated.

Further examples of this type are those of the reactions of thionemethiodides with amines such as aniline and hydrazine[42]. In these cases, the loss of methanethiolate ion is followed by loss of a proton.

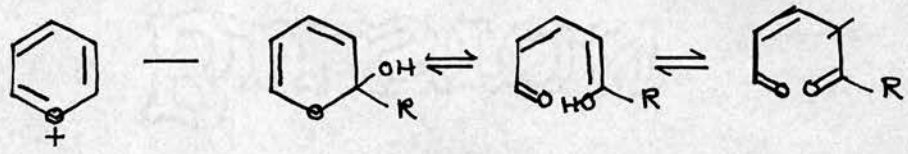
B). Nucleophilic attack on a nuclear sulphur atom without ring fission. The reaction of 2,4,6-triphenylthiopyrylium perchlorate (c1) with phenyllithium produces I,2,4,6-tetraphenylthiabenzene (c11)[48a,b,c].



(c1) (c11)

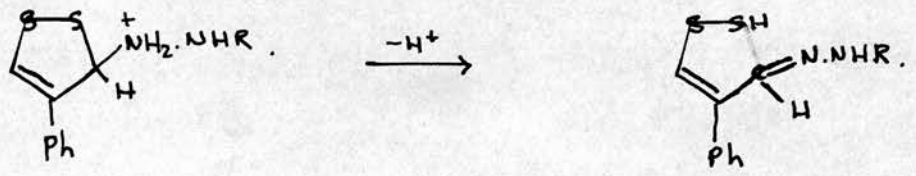
No examples are known of this type of attack in the dithiole series.

C). Nucleophilic attack on a nuclear carbon atom with ring fission. This is the well known ring-chain tautomerism of many heterocyclic pseudobases.



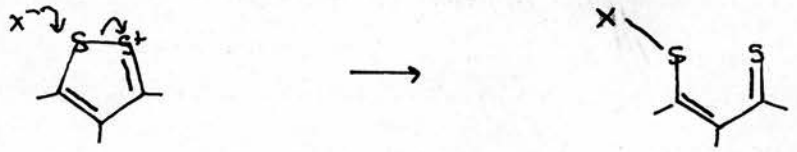
This type of reaction presumably occurs with the action of hydroxide on the I,2-dithiolium cation [7], mentioned in the introduction. The intermediate pseudobase formation is followed by ring cleavage to an aldehydic dissulphide.

The reaction of the I,2-dithiolium cation with hydrazines also produces these intermediates (c111)(c1V). In this case, however, there is loss of sulphur and a substituted pyrazole is the product obtained.[7]



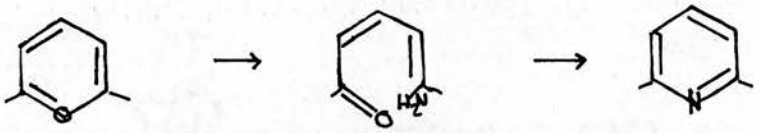
(c111) (c1V)

D). Nucleophilic attack on a ring sulphur atom with ring fission. No precedents for this type of reaction are known, but it is easy to envisage that a I,2-dithiolium cation might react as follows.

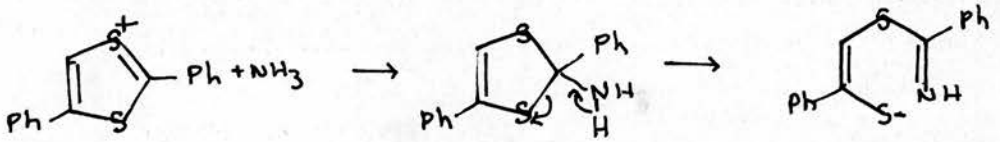


E). Type C).reaction followed by replacement of a heteroatom.

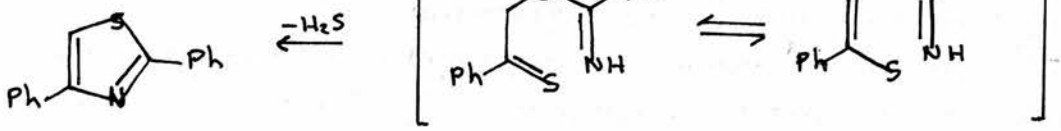
e.g.



The synthesis of diphenyl thiazole (cv) from 2,4-diphenyl-I,3-dithiolium perchlorate (LIVa)(11) and ammonia is probably this type of reaction.

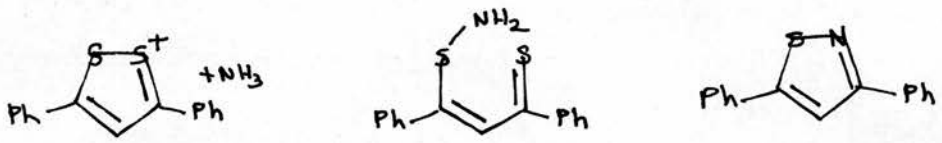


(LIVa)



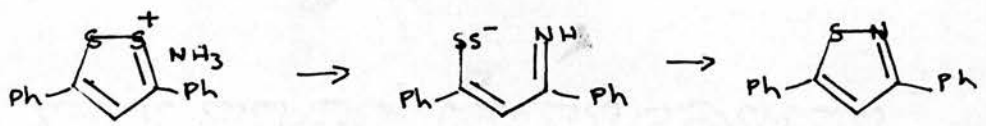
(cv)

F). Type D). reaction followed by replacement of a heteroatom.
It is possible that the formation of 3,5-diphenylisothiazole (LXXXVI) from 3,5-diphenyl-I,2-dithiolium perchlorate follows [11] this scheme.



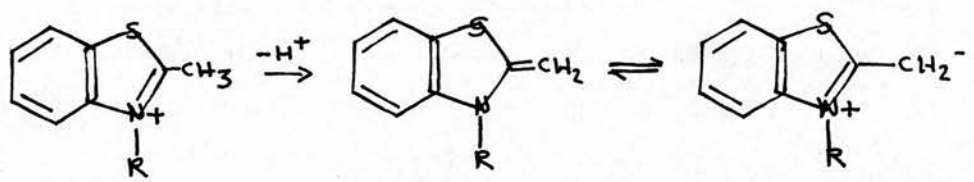
(LXXXVII)

It is also possible,however, that it is the type E). indicated above.



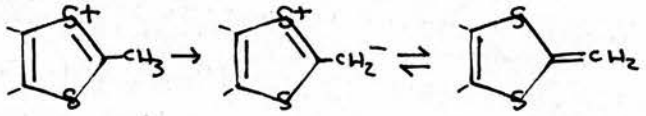
(LXXXVII)

G). Removal of a proton from a side chain methyl or methylene group.
e.g.



In the I,3-dithiolium series, an example of this is provided by the 2-benzyl-4-phenyl compound (LXXX) of Kirmse and Horner[37]. Treatment of this with base produced the 2-benzylidene-compound (LXXI).

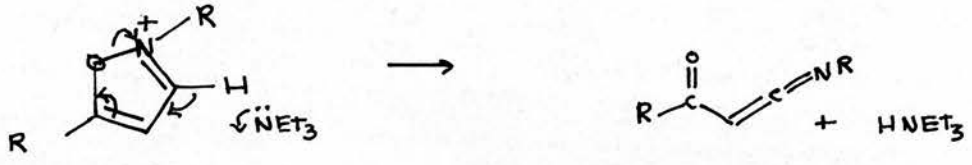
Robertson[11] and Wizinger[36] have condensed reactive methyl substituents with aldehydes to produce substituted vinyl-dithiolium salts. There is an intermediate methylene compound (CVI) in the reaction which is stabilised by resonance.



(CVI)

H). Removal of a proton from a nuclear carbon atom.

e.g.



(CVII) (CVIII)

The N-ethyl-5-phenylisoxazolium cation (CVII), when treated with triethylamine, produced the α ketoketenimine (CVIII)[49].

Also, under very mild conditions, thiazolium salts (CIX) readily form the zwitterions (CX) by removal of a proton[50].

(CIX) (CX)

This type of reaction is unreported in the dithiolium series.

MATERIALS.

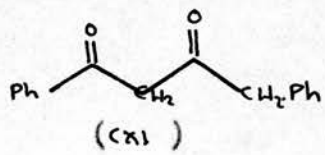
A number of the dithiolium salts required in this invesigation were not previously known, and were prepared by extensions of known methods. Also, some known dithiolium salts were prepared by methods different to those described in the literature. These syntheses and some that failed are described below.

Preparations of I,2-Dithiolium Salts.

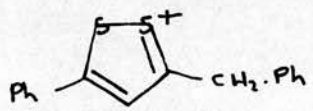
Attempts were made to prepare I,2-dithiolium salts or dithiole derivatives from phenylmalondialdehyde, nitromalondialdehyde and oxaloacetic ester by reaction with hydrogen disulphide in benzene saturated with hydrogen chloride. Only nitromalondialdehyde produced a solid product. Addition of hydrogen disulphide produced first a bright green colour, followed by the rapid formation of an orange precipitate. This was insoluble in most organic solvents except dimethyl-formamide and could not be purified. It had no definite melting point, and slowly turned brown on heating. No nitro groups were identifiable in it by Infra-red spectroscopy.

The results tend to confirm the view[11] that the above method of synthesis of dithiolium salts fails where there is no stabilizing aryl group attached to one of the carbonyl groups.

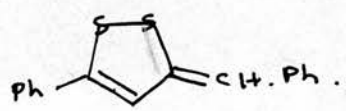
Phenylbenzoylacetone (CXI), prepared by the method of Bulow and Grotowsky[51] reacted under the usual conditions with hydrogen disulphide. 3-Benzyl-5-phenyl-I,2-dithiolium chloride was quickly formed. The salt was converted to its perchlorate (CXII) in glacial acetic acid. In alcoholic solution the salt rapidly turned orange, probably owing to formation of the anhydrobase (CXIII) by loss of a proton from the benzyl group.



(CXI)



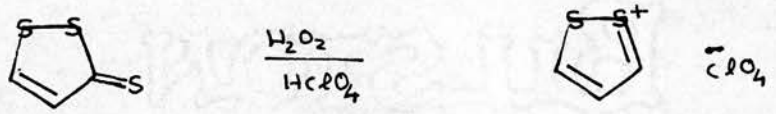
(CXII)



(CXIII)

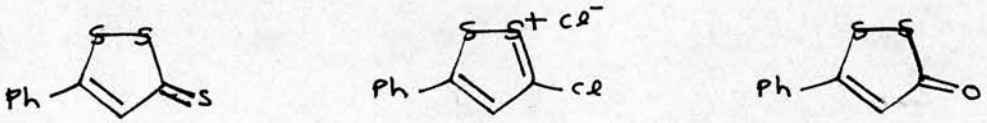
Klingsberg[6] prepared the parent I,2-dithiolium cation by peracetic acid oxidation of 3-thio-I,2-dithiole-5-carboxylic acid, but there seemed no reason why the reaction should not be carried out in the absence of the carboxyl group from the outset.

Accordingly, I,2-dithiole-3-thione (VII), prepared by the method of Mayer and Kubasch[52] was oxidized in acetic acid solution with three equivalents of 30% hydrogen peroxide. Addition of perchloric acid followed by ether precipitated the I,2-dithiolium cation as its perchlorate (III). It was found desirable to perform this reaction at room temperature. If the mixture was allowed to warm to above 40°C. the product was less pure.



(VII) (III)

Chlorination of 5-phenyl-I,2-dithiole-3-thione (XVIIa) in glacial acetic acid suspension proceeded with lightening in colour of the solution. Addition of ether precipitated 3-chloro-5-phenyl-I,2-dithiolium chloride (CXIV) which was converted to the perchlorate in glacial acetic acid. The chloro- compound dissolved in warm water and ethanol, but the solutions rapidly became yellow, because of hydrolysis to the parent dithiolone (CXV).



(XVIIa) (CXIV) (CXV)

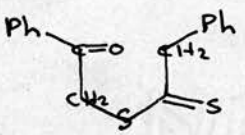
On keeping, the compound slowly turned greenish brown, suggesting decomposition. A satisfactory analysis for sulphur and chlorine was not obtained, but subsequent reactions indicated that the compound was substantially the chloro-dithiolium perchlorate.

The yields of chloro-dithiolium salts were quite low (ca 30%), suggesting that some side reaction was also involved, but no other product was isolated.

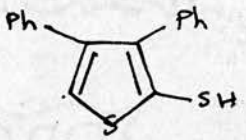
Preparations of I,3-Dithiolium Salts.

Since I,3-dithiolium salts have been prepared by the acid catalysed cyclisation of oxoalkyl-dithiocarboxylates[11], it was thought that this method might be applicable to the preparation of the known 2-benzyl-4-phenyl-I,3-dithiolium cation[37] (LXXX)

Accordingly, phenacyl phenyl(dithioacetate) (CXVI) was prepared by the reaction of equivalent quantities of phenacyl bromide with sodium phenyl-(dithioacetate) in aqueous ethanol at 0°C. The dithioester precipitated on standing. Reaction of the two compounds in boiling ethanol produced a different product, whose analysis corresponded to the molecular formula $C_{16}H_{12}S_2$. This compound, which was probably 3,4-diphenylthiophen-2-thiol (CXVII) or a tautomer, could have been formed from the dithioester by base-catalysed elimination of water.



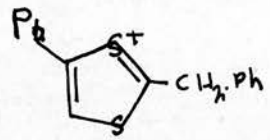
(CXVI)



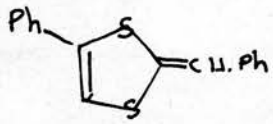
(CXVII)

Support for this structure was provided by the formation of meso - 2,3-diphenyl butane on desulphurisation of the compound with Raney nickel.

The dithioester cyclised easily in ether solution saturated with hydrogen sulphide, using a boron trifluoride - ether complex as the catalyst. Treatment of the precipitated salt with perchloric acid in glacial acetic acid afforded the known 2-benzyl-4-phenyl-I,3-dithiolium perchlorate (LXXX) which on treatment with sodium carbonate solution, gave the known 2-benzylidene-4-phenyl-I,3-dithiole (LXXI).

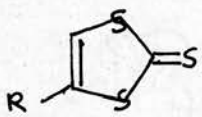


(LXXX)

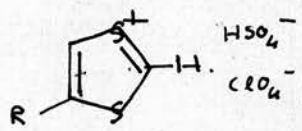


(LXXXI)

Since I,3-dithiole-2-thiones have similar properties to the I,2-thiones, it seemed possible that on peracetic acid oxidation, they too should yield dithiolium salts. Accordingly I,3-dithiole-2-thione (VIII) was treated in acetic acid solution with three equivalents of 30% hydrogen peroxide. After twenty minutes, addition of perchloric acid followed by ether precipitated I,3-dithiolium perchlorate (IV). Similarly, 4-phenyl-I,3-dithiole-2-thione (CXVIII) was oxidized to the 4-phenyl-I,3-dithiolium cation, isolated as its hydrogen sulphate. The hydrogen sulphate was converted to the perchlorate in glacial acetic acid.

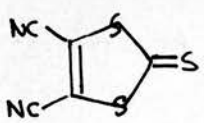


(VIII) a R = H
(CXVIII) b R = Ph

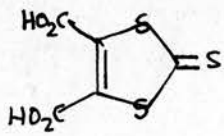


(IV) a R = H
(CXIX) b R = Ph.

An acid hydrolysis of 4,5-dicyano-I,3-dithiole-2-thione (CXX), prepared by the method of Wolf, Degener and Petersen[53] produced 2-thio-I,3-dithiole-4,5-dicarboxylic acid[CXXI], which however, failed to yield a dithiolium salt on treatment with peracetic acid. The thione also failed to produce a methiodide.



(CXX)



(CXXI)

Possibly the expected cation is destabilised by the electron-attracting carboxyl groups.

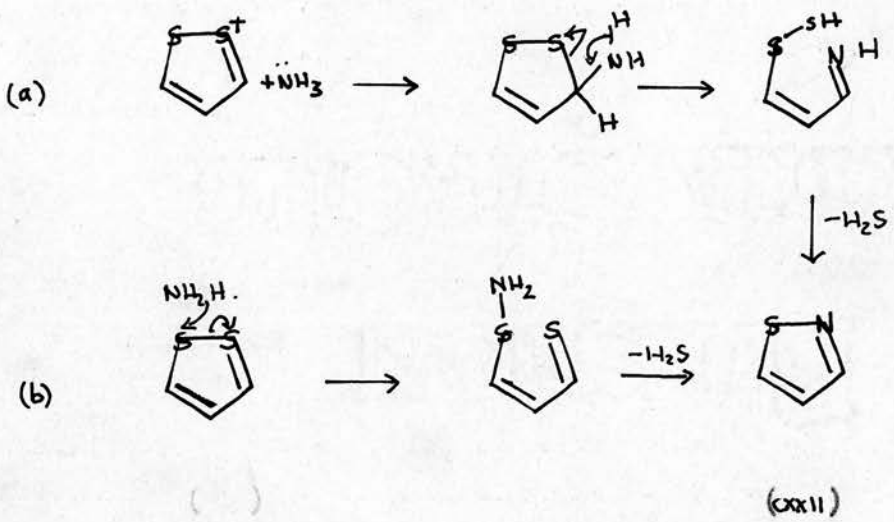
In such a cation, the carboxyl groups would not be attached to carbon atoms possessing carbonium ion character, and would probably not, therefore, be spontaneously lost as in the related reaction of 5-thio-1,2-dithiole-3-carboxylic acid (XIII) described by Klingsberg[6].

REACTIONS OF I,2-DITHIOLIUM SALTS WITHOUT REPLACEABLE SUBSTITUENTS.

Three I,2-dithiolium salts, the 4-phenyl (XVIIIb), 3,5-diphenyl (XXIa) and parent compound (III), which were chosen for their symmetry, were allowed to react with a variety of nucleophilic reagents.

I,2-Dithiolium perchlorate (III).

(I). Reaction with ammonia. The reaction of this compound with ammonia might be expected to produce isothiazole (CXII), either by the mechanism(a) shown, or by one involving nucleophilic attack on sulphur(b)



(CXXII)

A reagent consisting of ammonium acetate in acetic acid has been used to convert pyrylium salts into pyridines, and it seemed likely that this would react similarly with the dithiolium salt. When the perchlorate (III) was allowed to react with the reagent, hydrogen sulphide was evolved and the reaction mixture turned yellow. No isothiazole could be isolated from it. It may be that the quantities used (0·25g of perchlorate) were too small compared with the volume of solvent (20 ml) and that any isothiazole formed was lost in the working up procedure. Another reason for this failure could be that the intermediates in the reaction are too unstable and decompose by alternative pathways.

(II). Reaction with diethyl sodiomalonate. From the reaction of the perchlorate with diethyl sodiomalonate only one product was isolable. This was purified by chromatography and proved to be I,2-dithiole-3-thione(VII)

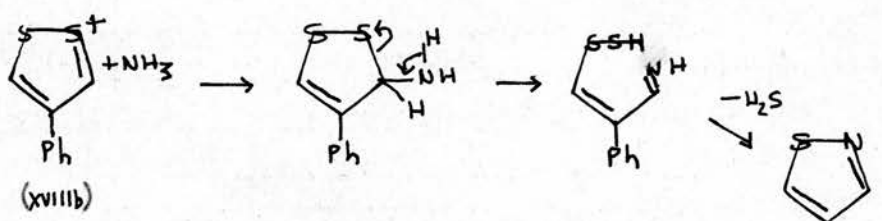
(VII). The reaction is clearly analogous to that of the 4-phenyl-I,2-dithiolium cation discussed below.

4-Phenyl-I,2-dithiolium perchlorate. (XVIIIb)

(I). Reaction with ammonia. Reaction of the perchlorate with ammonium acetate in acetic acid caused evolution of hydrogen sulphide, and from the solution was obtained a compound whose analysis corresponded to that required for 4-phenyl-isothiazole (CXXIII) and which had an ultraviolet spectrum consistent with this structure. The compound was purified via its perchlorate.

When the reaction was attempted, by passing dry ammonia into a boiling suspension of the perchlorate in benzene, some 4-phenyl-isothiazole was isolated, but the product obtained in greater yield was a yellow powder, whose analysis corresponded to that of a bis-(4-phenyl-I,2-dithiol-3-yl) sulphide (CXXIV). (Yield = 60%). Confirmation of this structure was provided by the treatment of the sulphide with acid, whereby the original dithiolium salt was regenerated with evolution of hydrogen sulphide. This sulphide (CXXIV) is probably formed by reaction between hydrogen sulphide and ammonia to produce hydrosulphide anion, which attacks a dithiolium cation to produce a -3-mercaptodithiole. This could lose another proton and attack another dithiolium cation to produce the bis-dithiolyl sulphide. The formation of the latter is analogous to the formation of di-tropyl sulphide from the tropylium cation and hydrogen sulphide in the presence of ammonia (54,55.)

The reactions may be represented by the following scheme.

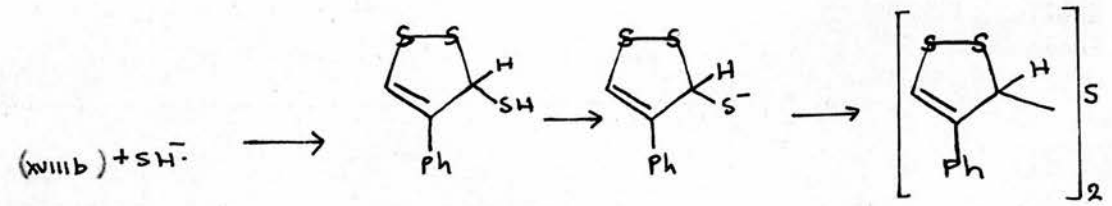


(XVIIIb)

Now the eliminated hydrogen sulphide reacts with ammonia, with attack on more dithiolium salt.

(CXXII)

$$H_2S + NH_3 \longrightarrow NH_4^+ + SH^-$$

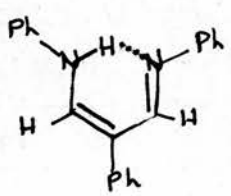


(cxxiv)

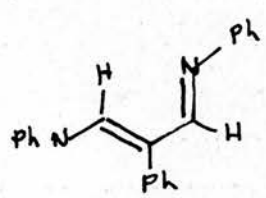
Hydrogen sulphide would not be sufficiently ionised in acetic acid to produce the sulphide, consequently the isothiazole is the main reaction product in this solvent.

This scheme provides for the formation of one mole. of sulphide and one of isothiazole from three moles. of the dithiolium salt. Hence the maximum yield of sulphide should be 67%; the actual yield of 60%, therefore, supports the suggested reaction scheme.

(II). Reaction with aniline. The perchlorate reacted with aniline in ethanolic solution or benzene suspension to produce a yellow perchlorate. Sulphur was completely eliminated as hydrogen sulphide. The free base was produced by shaking the perchlorate in acetone with sodium hydroxide solution. It is identical to a sample of cis —phenylmalondialdehyde dianil (cxxv), prepared along with the trans-form (cxxvi), by reaction of phenylmalondialdehyde with aniline.



(cxxv)



(cxxvi)

The nuclear magnetic resonance spectrum of the supposed cis form shows a sharp peak at I·97τ and a group of peaks between 2·5 and 3·0τ. If the latter one is taken to represent the fifteen phenyl protons, the peak at I·97τ is due to two protons. No other absorptions were

found between 0 and 10τ, but a compound with seventeen protons is impossible, so it must be assumed that the absorption of the remaining proton lies outside the range investigated. (This is quite possible for chelated NH.) This spectrum is consistent with that to be expected for a cis-dianil, because the two methine protons would be rendered equivalent by rapid tautomerism of the chelated structure.

In place of the singlet at 1·97τ, the spectrum of the supposed trans-dianil shows two equivalent doublets (J = 3·6 c.p.s.) at 0·38τ and 2·33τ. The former is probably due to the methine proton on the azomethine carbon atom (aldehydic) and the latter to other methine protons. These are not equivalent since the tautomerism is too slow.

p-Toluidine reacted with the perchlorate to give a similar derivative.

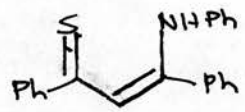
When 4-phenyl-1,2-dithiolium perchlorate was boiled under reflux in N-methyl aniline, a violet dye was formed. The dye could not be purified, but it would seem likely that it is related to the dyes (lxxxii) produced by Klingsberg [43] from dimethyl aniline and 3- and 4-phenyl-1,2-dithiolium perchlorates.

(III). Reactions with other anions. Viz. ethoxide, cyanide, hydrosulphide, and the anions of diethylmalonate and nitromethane produced extensive decomposition of the molecule. In all cases, brown oily gums were formed, from which only 4-phenyl-1,2-dithiole-3-thione (xviib) was isolated. These results tend to confirm the observation of Klingsberg[40], that, under basic conditions, at temperatures above -20°C., dithiolium salts, unsubstituted in the 3- position, yield the corresponding thiones. Possibly if reaction had been carried out at temperatures below -20°C, addition would have been more successful.

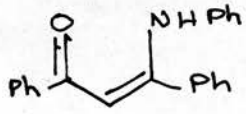
Klingsberg[40] has suggested that the thione arises by attack of sulphur, formed by decomposition of a portion of the dithiolium salt, on the remaining portion of the salt. In support of this view, he has shown that the thione is formed in high yield by the action of sulphur on the dithiolium salt in boiling pyridine.

3-5-Diphenyl-I,2-dithiolium perchlorate (xxiq).

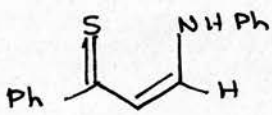
(I)a Reaction with aniline. Aniline reacted with the perchlorate in ethanol to produce a red compound $C_{21}H_{17}NS$. A small amount of sulphur was also isolated from the reaction mixture. The compound was shown to have the structure (cxxvii) by synthesis from 3-anilino-I,3-diphenylprop-I-one-3-one (cxxviii)(the monoanil of dibenzoylmethane) and phosphorus pentasulphide.



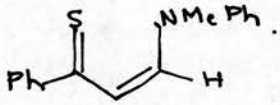
(cxxvii)



(cxxviii)



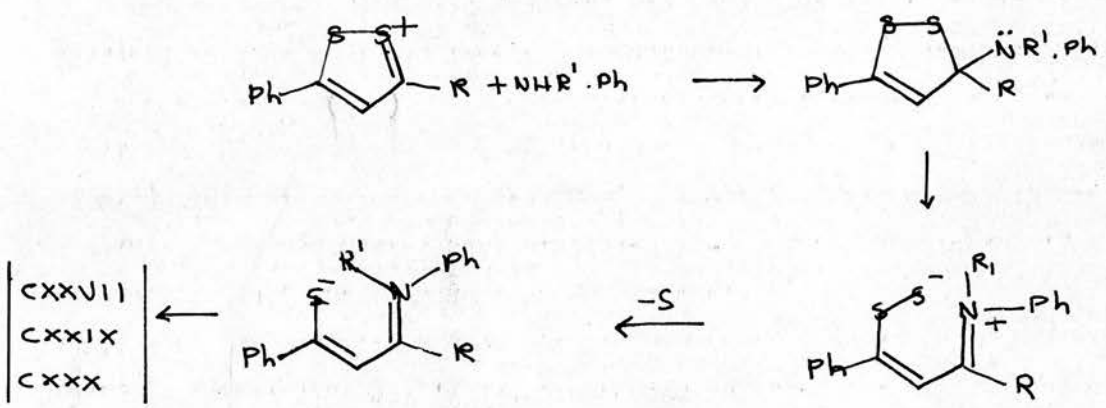
(cxxix)



(cxxx)

Similar compounds (cxxix) and (cxxx) were obtained by treatment of 3-phenyl-I,2-dithiolium perchlorate with aniline and N-methyl aniline respectively.

The visible and ultraviolet spectra of these three compounds are extremely similar (Fig.3), showing that they have a similar constitution. This indicates that the compounds (cxxvii) and (cxxix) exist in the anilino-thione form, and not in the tautomeric mercaptoanil forms, since the compound (cxxx) is incapable of such tautomerism. The ultraviolet spectrum of the latter shows some flattening of the maxima compared with the other compounds (cxxvi) and (cxxix), but this may be caused by the lack of hydrogen bonding. Failure to detect N - H stretching absorptions in the infrared spectra of compounds (cxxvii) and (cxxix) suggests that intramolecular hydrogen bonding occurs between nitrogen and sulphur and that the compounds are therefore this cis form, with relation to the double bond and not the possible isomeric trans forms, since the latter are incapable of internal hydrogen bonding. The compounds are probably formed by the following mechanism :-

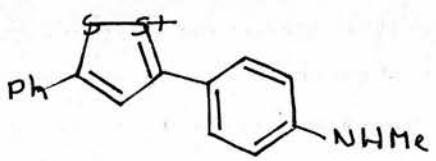


No reaction occurred between 3,5-diphenyl-I,2-dithiolium perchlorate and N-methyl-aniline in boiling ethanol. This may be because the bulky phenyl group in the dithiolium nucleus hinders the addition of the N-methyl-aniline.

These reactions are obviously similar to that producing cis phenyl-malondialdehydedianil from 4-phenyl-I,2-dithiolium perchlorate. The intermediate anilino-thione here however, is a thio-aldehyde, which would be expected to be much more reactive than the thiones (CXXIX type) It therefore reacts with more aniline and is not isolated.

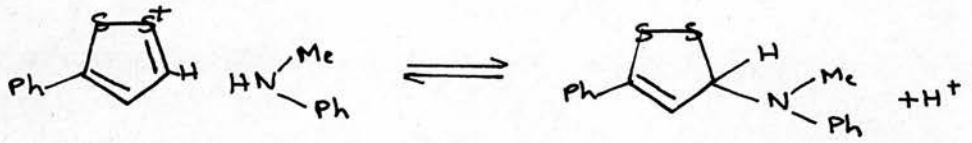
When N-methylaniline was heated with 3,5-diphenyl-I,2-dithiolium perchlorate in the absence of a solvent, a violet dye was produced. The dye was probably related to the benzothiapyrylium salt (CXXXII) obtained as described below from N,N-dimethyl-aniline-and the perchlorate.

Reaction of 3-phenyl-I,2-dithiolium perchlorate with N-methylaniline in hot ethanol also produced a violet dye, which was obtained crystalline, but the analysis of this compound indicated a structure of the type (CXXXI), similar to those of the dyes (CXXXII) obtained by Klingsberg[43] from dithiolium salts and tertiary aromatic amines.



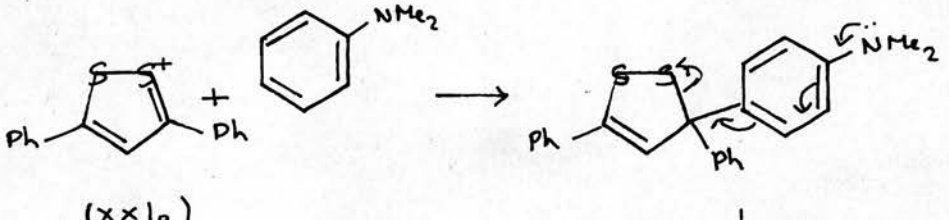
(CXXXI)

Thus the reaction of methylaniline with the 3-phenyl-I,2-dithiolium perchlorate produced two compounds, depending on the temperature of the reaction mixture. Even in the cold, a little of the dye was produced, as well as the anilino-thione (cxxx). This observation suggests that the equilibrium

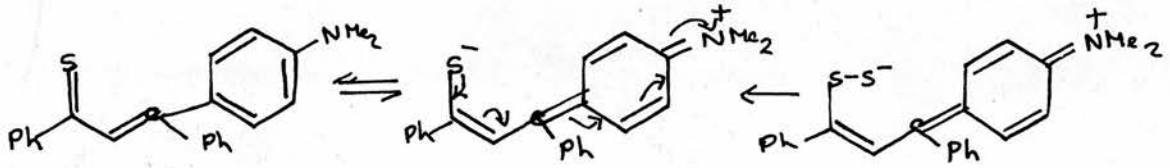


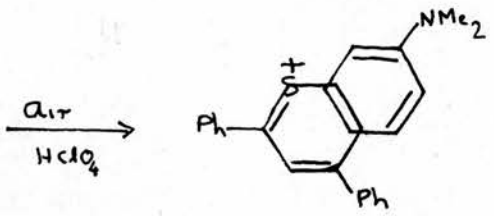
is displaced to the left at higher temperatures, and that electrophilic attack by the dithiolium cation on the p-position of the N-methylaniline (leading, on subsequent oxidation, to the dye cation) is facilitated at these temperatures. At the lower temperatures, this electrophilic substitution is evidently insufficiently rapid to compete with decomposition of the methylanilinodithiole to give the red thione (cxxx).

b) Reaction with N,N-dimethylaniline. The reaction of dimethylaniline with 3,5-diphenyl-I,2-dithiolium perchlorate was effected by heating the two compounds together in the absence of a solvent. The mixture quickly became purple and, on working up, a violet perchlorate was isolated. The analysis of this compound corresponded to that required for the benzothiapyrylium perchlorate (cxxxii). This could have been formed by the following series of reactions.



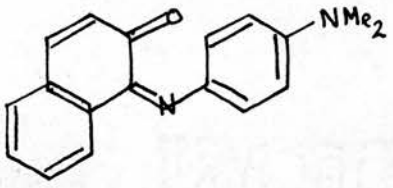
(XXIa)



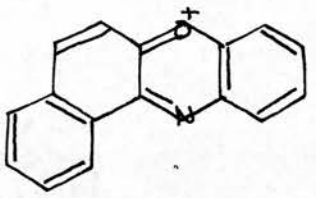


(CXXXII)

The structure of the dye (CXXXII) formed in the reaction still awaits rigorous proof, but the last stage in the suggested mechanism is related to the known formation of "Meldola's Blue" (CXXXIV) by ring closure of a similarly constituted ketone (CXXXIII).



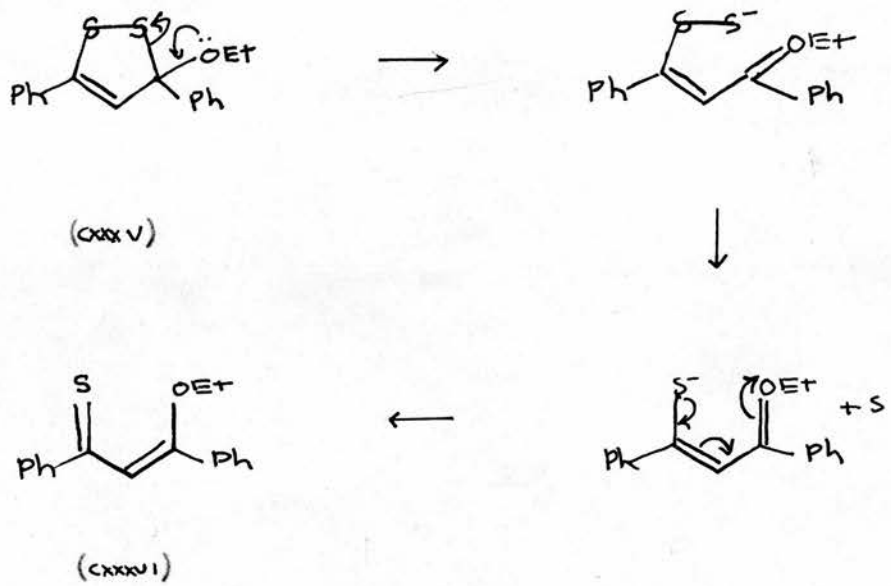
(CXXXIII)



(CXXXIV)

The reactions described above, producing the dyes (CXXXI) and (CXXXII) are of a recently investigated type, involving electrophilic substitution by aromatic cations. Other examples of such reactions are those of flavylium cations[56], benzodithiolium cations[36], and of I,2-[30] and I,3-[43] dithiolium cations with dimethylaniline.

(II). Reaction with ethoxide ion. Reaction of the perchlorate (XXIa) in ethanol with sodium ethoxide produced the ethyl ether (CXXXV). The compound could be chromatographed satisfactorily on deactivated alumina, but on activated alumina it decomposed to give a red product which failed to give consistent analytical results, particularly for sulphur. While the ethyl ether was converted into the original perchlorate on treatment with perchloric acid, the red compound was not so converted, indicating that widespread changes had occurred in the molecule. It is possible that the red solid was the ethoxythione (CXXXVI) contaminated with sulphur, produced by catalytic decomposition on alumina of the original ethyl ether.



(CXXXV)

(CXXXVI)

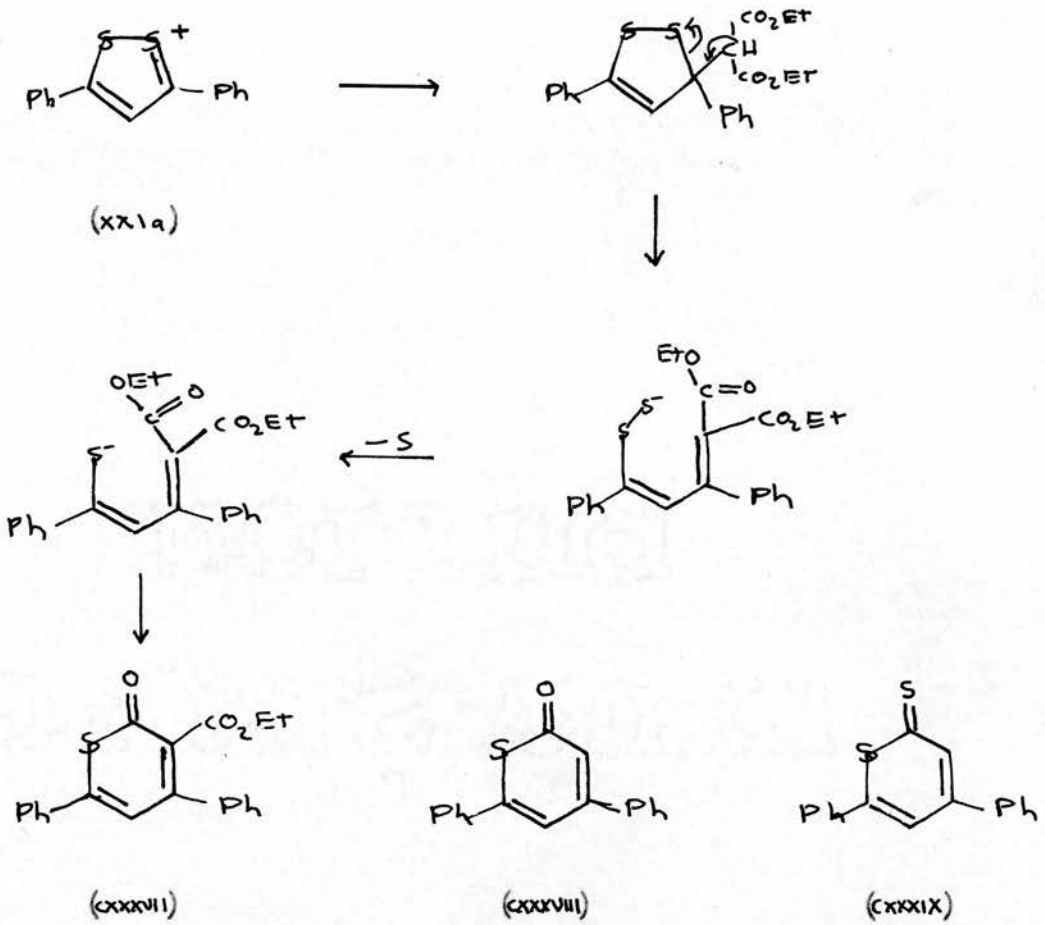
These transformations resemble those which must occur during the reaction of the 3-phenyl-I,2-dithiolium salt with N-methylaniline to form the analogous red N-methylanilino-thione (CXXX).

(III). Reaction with cyanide ion and p-toluenethiolate anion. Reaction of the perchlorate (XXIa) with sodium cyanide in ethanol produced only oils which could not be crystallised. Infra-red spectroscopy showed the presence of cyano groups, but it seems unlikely that the product was the expected 3-cyano-3,5-diphenyl-I,2-dithiole since this would probably be quite stable and crystalline. It is possible that nucleophilic attack occurred instead at one of the sulphur atoms, since it is known that the nucleophilicity of cyanide ion, relative to most other ions, is higher when attacking a sulphur atom than when attacking a carbon atom[57].

Reaction with the p-toluenethiolate anion, which also possesses a high sulphur nucleophilicity, likewise led to extensive decomposition and no pure product could be isolated.

(IV). Reaction with diethyl sodiomalonate. When the perchlorate was allowed to react with diethyl sodiomalonate in anhydrous ether, the solution became red, and then bright green. Evaporation yielded a pale yellow product which was not reconverted into the original cation on treatment with acid. The analysis of this compound suggested that it

might be 3-ethoxycarbonyl-4,6-diphenyl-thiopyran-2-one (CXXXVII), which could be formed by the following reaction scheme :-



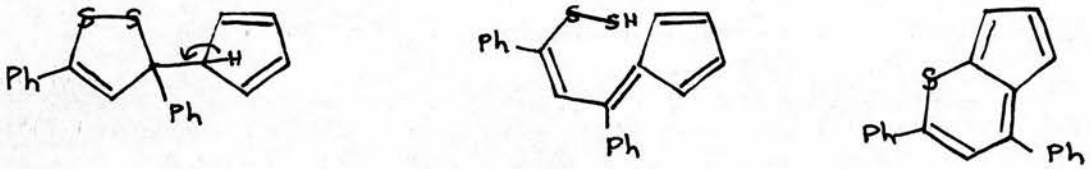
(XXIa)

(CXXXVII) (CXXXVIII) (CXXXIX)

The compound was hydrolysed and decarboxylated to give 4,6-diphenyl-thiopyran-2-one (CXXXVIII) by boiling in glacial acetic acid containing 20% of sulphuric acid. This thiopyrone was sulphurised in boiling carbon disulphide with phosphorus pentasulphide to produce the known 4,6-diphenyl-thiapyran-2-thione (CXXXIX). A further proof of the structure of the thiopyrone (CXXXVIII) was provided by its reaction with phenyl magnesium bromide, followed by perchloric acid to produce the known[60] triphenylthiapyrylium perchlorate.[61]

(V). Reaction with sodiocyclopentadiene. Pyrylium salts and pyridinium salts react with the sodium salt of cyclopentadiene to produce azulenes[58a,b]. It therefore seemed possible that the reaction of sodiocyclopentadiene

with dithiolium salts would produce pseudoazulenes according to the following scheme.



Such compounds would be expected to have a blue or violet colour. Addition of 3,5-diphenyl-I,2-dithiolium perchlorate to sodiocyclopentadiene in tetrahydrofuran did in fact produce a violet colour, but on working up, the mixture became brown, and the only product which could be isolated was an oil with a blue fluorescence.

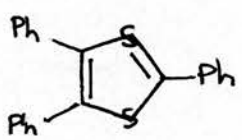
REACTIONS OF 1,3-DITHIOLIUM SALTS.

The symmetrical triphenyl-1,3-dithiolium perchlorate (LIV) was chosen for study in order to minimise the number of products.

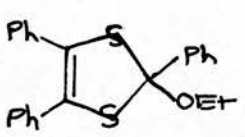
(I). Reaction with ethoxide ion and cyanide ion. Reaction with sodium ethoxide in ethanol produced the ethyl ether (CXL). This pale yellow compound lost the ethoxy group and was converted into the original cation on acidification in ethanolic or acetic acid solution.

Reaction of the perchlorate with sodium cyanide in ethanol produced the expected nitrile (CXLI) together with some of the ethyl ether. Evidently the cyanide ion is a sufficiently strong base to catalyse the reaction of ethanol with the dithiolium cation.

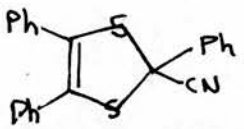
When the perchlorate was allowed to react with alcoholic sodium hydroxide, only the ethyl ether (CXL) was produced, probably owing to the greater nucleophilicity of ethoxide ion than of hydroxide ion. Pseudobases are known to exchange OR for OH readily, sometimes even by crystallisation from alcohols.



(LIV)



(CXL)



(CXLI)

(II). Reactions with ammonia. The product obtained by the reaction of the perchlorate with the ammonia molecule varied widely according to the medium in which the reaction was performed.

When anhydrous ammonia was passed into a suspension of the perchlorate in dry benzene, only one product was obtained, namely, 2-amino-2,4,5-triphenyl-1,3-dithiole (CXLII), the structure of which was shown by infra-red absorptions indicative of a primary amino-group and by its reaction with acids to regenerate the original cation.

When ethanol was used as a solvent, the products obtained were thio-benzamide, desoxybenzoin, and a yellow oil, chromatographically irresolvable, which yielded the original perchlorate on treatment with perchloric

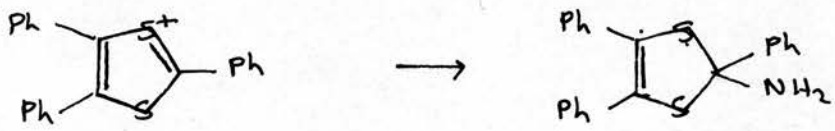
acid, and thus appeared to consist mainly of the aminodithiole. Reaction of the perchlorate in acetic acid with ammonium acetate caused a slight evolution of hydrogen sulphide and the formation of 2,4,5-triphenyl-I,3-dithiole (CXLV) and a yellow oil which on treatment with acid gave a mixture of 2,4,5-triphenyl-I,3-dithiolium perchlorate and 2,4,5-triphenylthiazolium perchlorate. In this case, therefore, the oil appeared to be a mixture of the amino dithiole and 2,4,5-triphenylthiazole (CXLIV).

2-amino-2,4,5-triphenyl-I,3-dithiole was stable in cold ethanol, but on boiling it decomposed with evolution of hydrogen sulphide to produce triphenyl-I,3-dithiole (CXLV), triphenylthiazole (CXLIV), desoxybenzoin, and thiobenzamide. A trace of sulphur was also found.

The structure of the triphenyl-I,3-dithiole was shown by its conversion into the original perchlorate on treatment with triphenylmethyl perchlorate, a compound which is known to abstract hydride ions readily (59), particularly when the reaction leads to a stable cation.

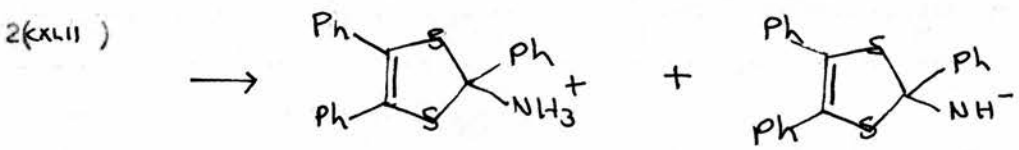
These experiments indicate that in hydroxylic solvents, the reaction with ammonia is very complex. It is probable that it follows the scheme outlined below :-

The initial reaction was undoubtedly the formation of the aminodithiole, which was the only product isolated when the reaction was carried out in the aprotic solvent, benzene.



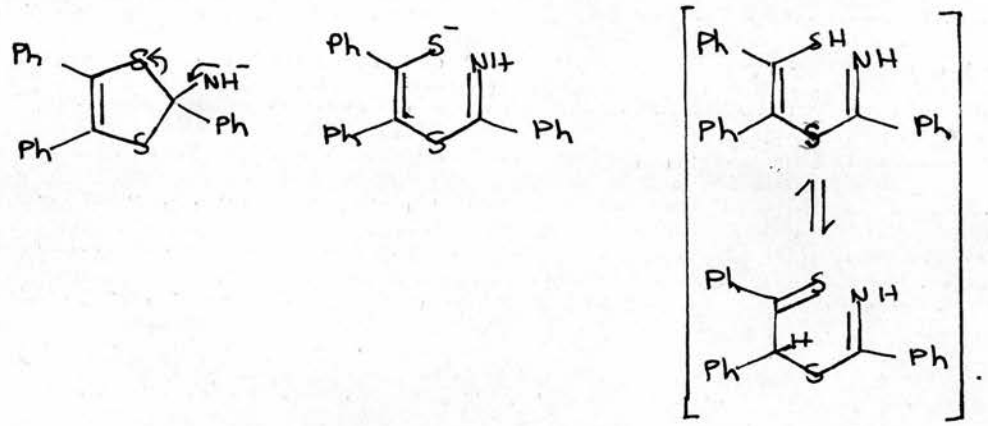
(LIV) (CXLII)

In a hydroxylic solvent such as ethanol, this aminocompound (CXLII) probably disproportionates to a very slight extent, by proton transfer.



(CXLIIa) (CXLIIb)

The cation (CXLIIIa) would lose ammonia to form the original triphenyl-I,3-dithiolium cation, while the anion (CXLIIIb) probably rearranges to the open-chain compound (CXLIII).

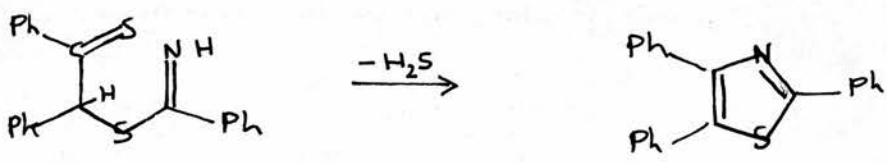


(CXLIII)

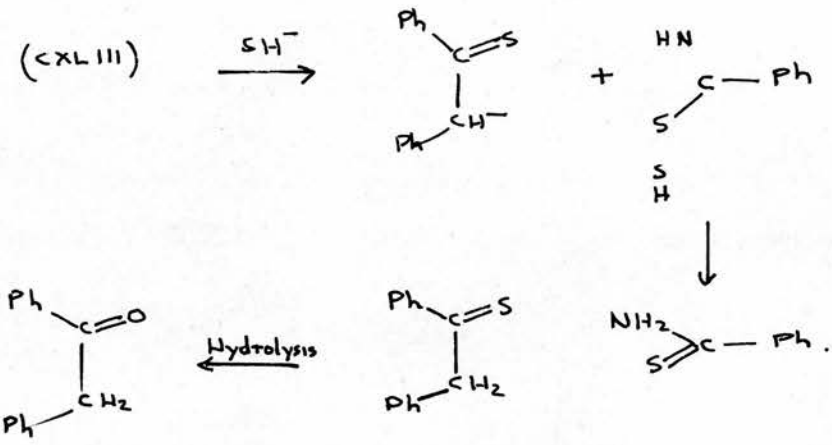
Such a compound (CXLIII) resembles the intermediate in the synthesis of thiazoles from thioamides and haloketones. It is probably therefore, the precursor of 2,4,5-triphenyl thiazole (CXLIV).

The formation of thiobenzamide by fission of the open-chain compound is readily envisaged, but the formation of desoxybenzoin implies that, at some stage, the desyl-sulphur bond is broken with the formation (complete or incipient) of a carbanion.

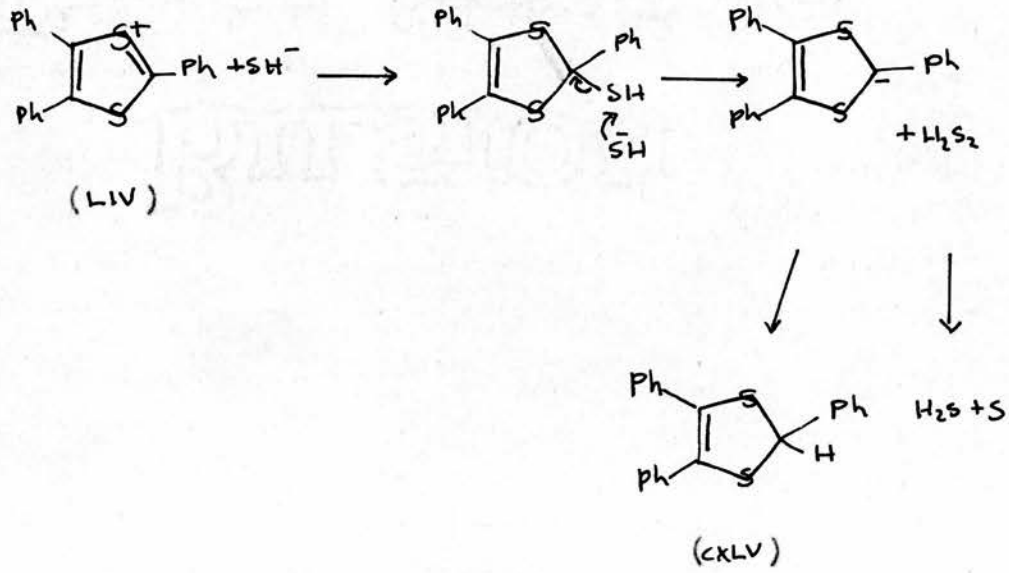
A search of the literature reveals that this type of fission is quite common in desythio-compounds (e.g. desyl mercaptan[61,62]) under basic conditions, and it has been suggested that the mechanism involves a nucleophilic attack on sulphur. One possible scheme for the transformations of the open-chain compound is outlined below.



(CXLIII) (CXLIV)



Hydrosulphide ion was shown to be responsible also for the formation of the triphenyldithiole since the compound was obtained in high yield by treatment of the dithiolium perchlorate with sodium hydrogen sulphide in ethanol. The mercaptodithiole is in all probability formed first; cleavage of this by a mechanism similar to that described above for desylthio-compounds would then give the dithiole.



(III). Reaction with phenylmagnesium bromide. An attempt was made to carry out a reaction between the triphenyl-1,3-dithiolium cation and phenyl-magnesium bromide in ether, but since the cation was insoluble

in ether, reaction did not occur easily. Only two products were isolated, triphenyl-1,3-dithiole and an oil which on treatment with acid gave the original cation (LIV). These are probably compounds formed by the water used in the working up process.

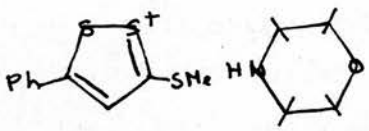
Since the ultra-violet spectra of the I,3-dithiole derivatives are similar, it follows that the substituents must be similarly placed in the dithiole ring, and since the amino group must be placed in the 2-position for the eventual formation of triphenyl thiazole from the aminodithiole (LXIII), it follows further that all are 2-substituted derivatives.

This eliminates the possibility that nucleophilic attack occurred at one of the sulphur atoms, as has been found for the attack of phenyl-lithium on the triphenylthiapyrylium cation[48]. Presumably this type of attack only occurs where the attacking group has a high sulphur nucleophilicity, or where it is too bulky to attack the carbon atom, since nucleophilic addition of ammonia or hydrosulphide is known to occur at the 2-position.

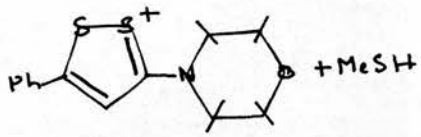
It is unfortunate that no phenyl addition product was isolated from the reaction of the cation (LIV) with phenylmagnesium bromide.

REACTIONS OF 1,2-DITHIOLIUM SALTS CONTAINING REPLACEABLE SUBSTITUENTS.

When a halogen atom or methylthio group is attached to the 3-position of a 1,2-dithiolium cation, or to the 2- position in the 1,3- series, nucleophilic attack at these positions can lead to replacement with elimination of hydrogen halide or methyl mercaptan. Thus the 3-chloro or 3-methylthio-5-phenyl-1,2-dithiolium cation condensed with morpholine to produce a morpholinodithiolium salt (CXLVI) which was isolated as the perchlorate.



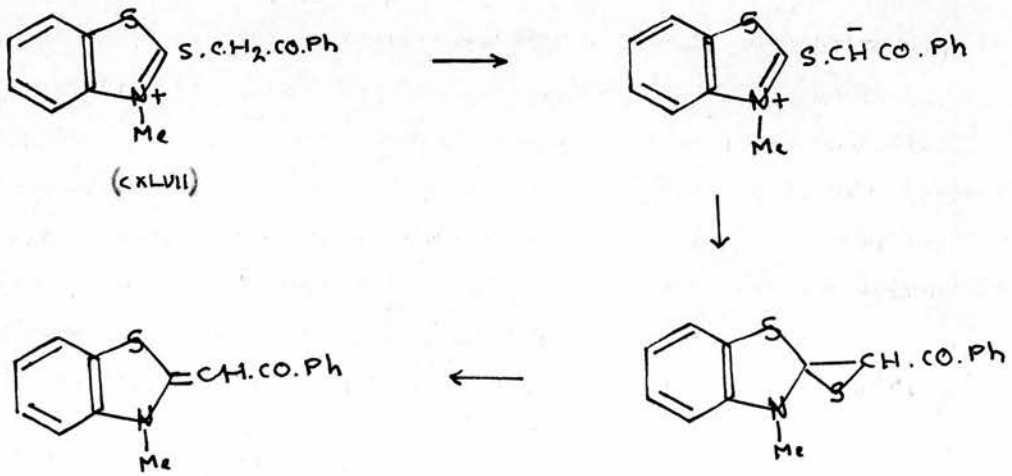
(LXXXVI)



(CXLVI)

Synthetical approaches to "thiothiophthenes" by nucleophilic substitution in the dithiole nucleus.

Treatment of the phenacylthiobenzothiazolium bromide (CXLVII) with triethylamine produces the phenacylidene-benzothiazoline (CXLIX)[63]. It has been suggested that a proton is removed from the methylene group and that intramolecular nucleophilic attack at the 2- position then leads to the episulphide (CXLVIII) from which a sulphur atom is extruded.



(CXLVII)

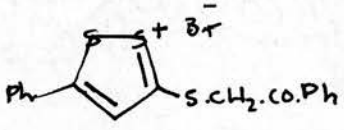
(CXLIX)

(CXLVIII)

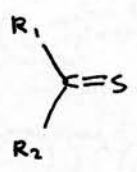
A similar reaction with 3-phenacylthio-I,2-dithiolium salts would give phenacylidenedithioles which could be sulphurised to "thiothiophthenes."

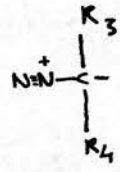
5-phenyl-I,2-dithiole-3-thione in nitromethane reacted with phenacyl bromide to produce the expected bromide (CL), which was converted to the perchlorate in glacial acetic acid. The perchlorate decomposed rapidly in alcoholic solution so its treatment with triethylamine was effected in glacial acetic acid. Precipitation with water produced an uncrystallisable red powder, which was purified by chromatography on alumina to give a red oil, which solidified in ethanol/petroleum ether to a red powder. The analysis of this did not correspond to the desired phenacylidenedithiole (CLIV) and could not be fitted to any resonable empirical formula.

Episulphide intermediates are known to be formed in the reactions of thiocarbonyl compounds (CLI) with diazo-compounds [64-73]. The final products are substituted ethylenes (CLII), formed in the same way as the phenacylidene compound (CLIV) by extrusion of sulphur.

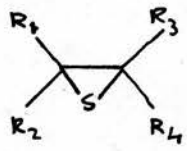


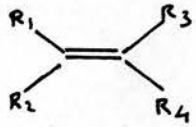
(CL)





(CLI)

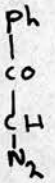




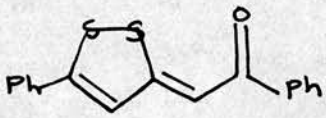
(CLII)

These reactions indicated that 3-phenacylidene-5-phenyl-I,2-dithiole might be produced by reaction between 5-phenyl-I,2-dithiole-3-thione and diazo-acetophenone (CLIII).

(XVIIb)



(CLIII)



(CLIV)

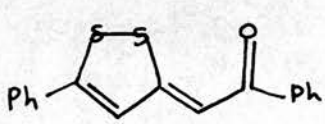
Diazoacetophenone, however, proved to be rather less reactive than was expected. It did not react with the thione in either boiling benzene, or on exposure to ultraviolet light; but when the two reactants were fused together, a vigorous reaction ensued, with evolution of a gas. When the resulting mixture was chromatographed on alumina, two main bands were obtained, one corresponding to unchanged thione, and the other to the desired phenacylidene dithiole (CLIV).

Attempts to prepare the phenacylidenedithiole by reaction of a methylthiodithiolium salt with acetophenone or with its sodio-derivative were unsuccessful, and so a milder method of generating the phenacyl anion was sought.

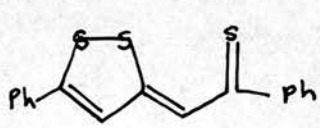
Monomethine cyanine dyes are formed by heating heterocyclic quaternary salts containing replaceable methylthio-groups with malonic acid in pyridine[94]. Decarboxylation of the malonic acid probably forms the anion $CH_2^- \cdot CO_2^-$ which then replaces a methylthio-group in the first stage of the reaction. It therefore seemed possible that the reaction of a methylthiodithiolium salt with decarboxylating benzoylacetic acid would give a phenacylidene dithiole.

When sodium benzoylacetate was allowed to react in boiling ethanol with 3-methylthio-5-phenyl-1,2-dithiolium iodide, methyl mercaptan and carbon dioxide were evolved, and the solution on evaporation yielded mainly a mixture of 5-phenyl-1,2-dithiole-3-thione and the phenacylidene-dithiole, separable by chromatography. Sulphurisation of the phenacylidene compound in boiling benzene with phosphorus pentasulphide afforded 5-phenyl-3-thiophenacylidene-1,2-dithiole (XXXIXb).

(LXXXVI)



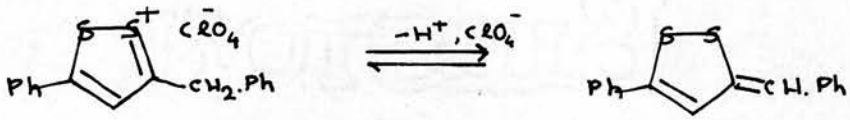
(CLIV)



(XXXIXb)

REACTIONS OF DITHIOLIUM SALTS CAPABLE OF FORMING ANHYDROBASES BY PROTON LOSS FROM A SIDE CHAIN.

I,2- and I,3-dithiolium salts bearing respectively 3- or 2- substituents containing α-ionisable hydrogen atoms would be expected to lose acid readily to form the anhydrobase, stabilised by resonance, as indicated in the introduction (compound IX.). 2-benzyl-4-phenyl-I,3-dithiolium salts are known[37] to lose a proton in this way, forming 2-benzylidene-4-phenyl-I,3-dithiole, and it is to be expected that 3-benzyl-5-phenyl-I,2-dithiolium perchlorate (CXII) will behave similarly to produce the anhydrobase (CXIII). A solution of the salt, when dissolved in ethanol, soon assumed an orange colour, indicating that the anhydrobase had been produced by dissociation.



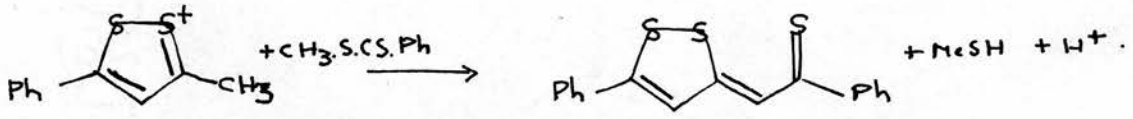
(CXII) (CXIII)

The actual preparation of the base was carried out by shaking the perchlorate with aqueous sodium carbonate solution or aqueous ammonia. No other reactions, such as isothiazole formation, or self condensation, were noted with the latter reagent.

Synthetical approaches to "thiothiaphthenes" by acylation of methylene-I,2-dithioles.

The exocyclic methylene of a methylenedithiole would be expected to possess a high π-electron density and might therefore be susceptible to attack by acylating reagents. Indeed, similar acylations are readily achieved in the 2-methylenebenzothiazolium series by simply allowing the 2-methylbenzothiazolium salt to react with an acyl chloride in pyridine[74]. The product in the dithiole series would be an acylmethylene dithiole which could be sulphurised to yield a "thiothiophthene". Unfortunately, treatment of 3-methyl-5-phenyl-I,2-dithiolium perchlorate with even weak bases such as pyridine caused the self-condensation described below, and the salt failed to react with benzoyl chloride in the absence of base, even after heating for one hour.

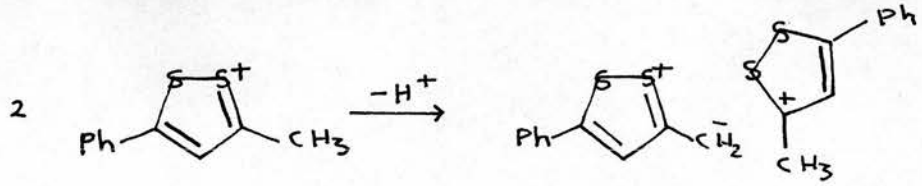
Thioacylation of the methyl group was eventually achieved by boiling the perchlorate under reflux with methyl dithiobenzoate in the absence of a catalyst or solvent other than the dithioester. This reaction parallels the thioacylation of 2-methylthiozolium salts with methyldithioacetate[75]. Methyl mercaptan was evolved, and perchloric acid eliminated to produce a brown oil. Resolution of this by chromatography produced 5-phenyl-3-thiophenacylidene-I,2-dithiole (XXXIXb)i.e. the diphenyl "thiothiophthene". A similar reaction with methyl benzoate failed. The explanation of this must lie in the greater polarity of the thiocarbonyl group in the dithioester relative to the carbonyl group in methyl benzoate. It is well known that thio- and dithio- esters are effective acylating agents. Reaction with the 3-methyl group is thus facilitated.



(XXIb) (XXXIXb)

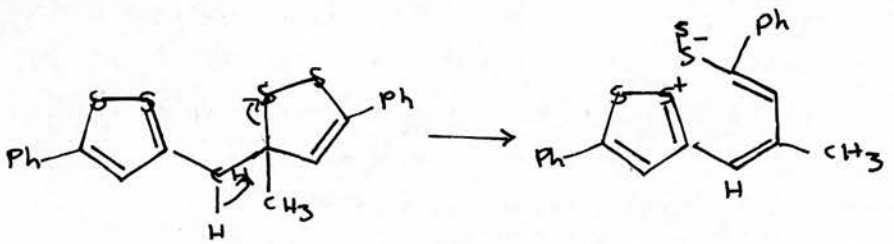
Self-condensation of 3-methyl-5-phenyl-I,2-dithiolium salts.

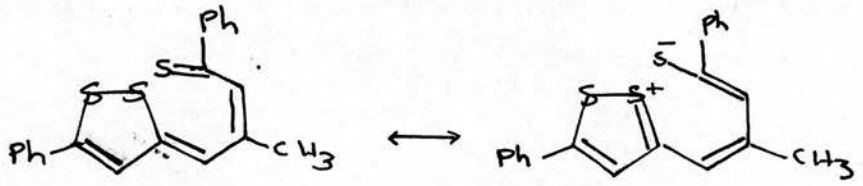
3-methyl-5-phenyl-I,2-dithiolium perchlorate (XXIb) in acetic acid solution in the presence of pyridine quickly produced a highly coloured purple compound which crystallised from nitromethane as dark violet needles. The analysis and absorbtion spectrum of this compound suggested that it might be either of the two products (CLVIIa) or (CLVIIb), produced by a self-condensation reaction of the dithiolium salt. A plausible mechanism for the formation of such a compound may be envisaged.



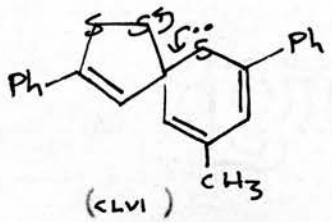
(XXIb)

The first stage involves nucleophilic attack of the anhydrobase on the nucleus of a second dithiolium cation. The usual fission of the dithiole ring followed by loss of sulphur would then lead to a mero-cyanine (CLV).



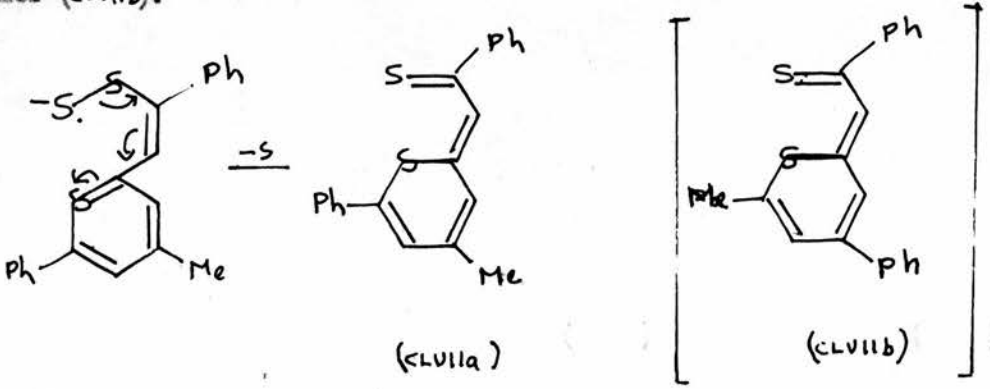


(CLV)



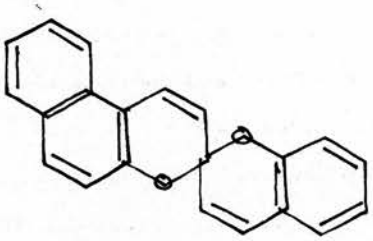
(CLVI)

Related merocyanines are formed by the reversible thermal isomerism of certain thermochromic spiropyrans e.g. ((CLVIII)⇌(CLIX) [82]), and it seems probable that the compound (CLV) would readily undergo ring closure to form the spiropyran (CLVI). Opening of the dithiole ring in this compound would then be followed irreversibly, by loss of sulphur to form the thiophenacylidenethiopyran (CLVIIa). Initial attack at the 5- position of the dithiolium cation would lead similarly to the isomer (CLVIIb).

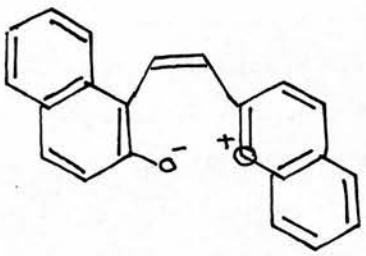


(CLVIIa)

(CLVIIb)



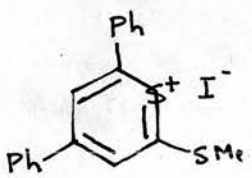
(CLVIII)



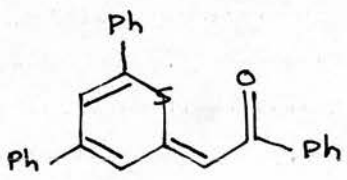
(CLIX)

It is most probable that the compound isolated should be formulated as (CLVIIIa). The carbon atom carrying the methyl group would be less hindered sterically for electrophilic attack on the methylene group of the anhydrobase than that attached to the phenyl group.

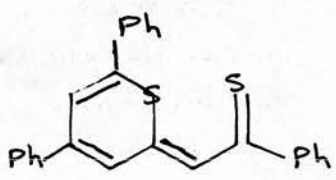
In order to obtain a related compound whose structure was more amenable to proof by synthesis, 3,5-diphenyl-I,2-dithiolium perchlorate was allowed to react in pyridene solution with an equivalent quantity of 3-methyl-5-phenyl-I,2-dithiolium perchlorate, thereby producing a compound whose analysis corresponded to that of 4,6-diphenyl-2-thiophenacylidenethiopyran (CLXII). The structure of this compound was proved from synthesis from 4,6-diphenyl-2-methylthio-thiopyrylium iodide (CLX) (prepared from 4,6-diphenylthiopyran-2-thione), which reacted in ethanol with sodium benzoylacetate to produce a ketone (CLXI). The latter afforded the compound (CLXII) identical with that obtained from the mixture of dithiolium salts, on sulphurisation in boiling benzene with phosphorus pentasulphide.



(CLX)



(CLXI)

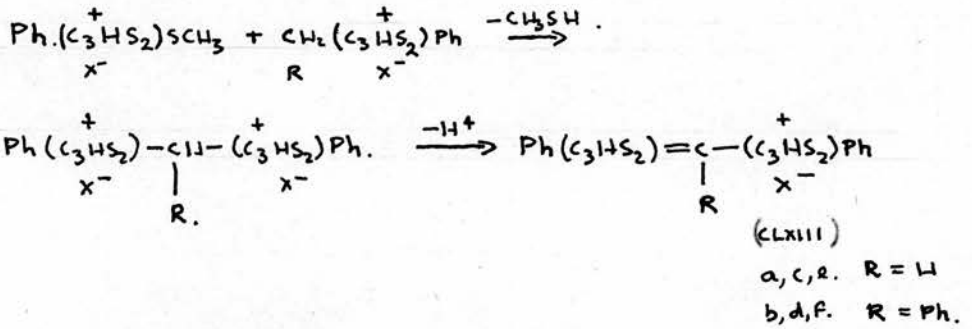


(CLXII)

Formation of cyanine dyes.

A further manifestation of the reactivity of methyl groups in cationic heterocycles is to be found in their reaction with the corresponding methylthio compounds to form cyanine dyes.

Wizinger has shown that cyanine dyes [34] are very readily formed by reactions of this type in the benzo-I,3-dithiolium series and it was therefore of interest to investigate their formation from mononuclear dithiolium salts according to the general reaction.



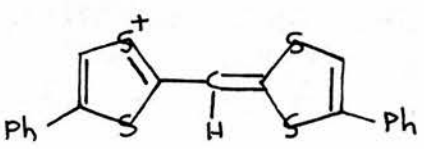
(CLXIII)

a, c, e. R = H

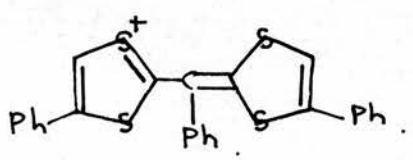
b, d, f. R = Ph.

Equimolar quantities of two phenyldithiolium salts, suitably substituted with methyl and methylthio groups respectively, were allowed to react together in glacial acetic acid. In the absence of a basic catalyst, the products obtained seemed to be a mixture of the starting materials, possibly double salts. When a drop of pyridine was added to the reaction mixture, an instantaneous purple colour was produced, and, on cooling the solution, the mono-methine cyanine dyes (CLXIII) were precipitated. These were highly crystalline violet salts, with a green reflex. Unfortunately, they were extremely difficult to purify. The necessity for a basic catalyst suggests that the mononuclear cations are less reactive than the benzo-I,2-dithiolium salts which react readily in acetic acid alone.

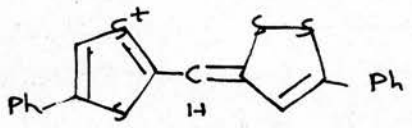
The six compounds shown below were prepared; the wavelength and logε values of the visible absorbtion maxima are shown in parentheses.



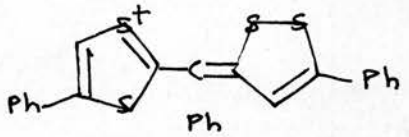
(CLXIII) a(525mμ logε=4·74)



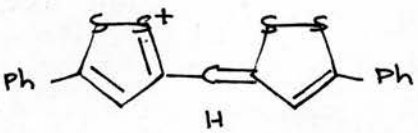
(CLXIII) b(528mμ logε=4·745)



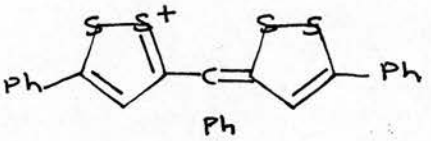
(CLXIII) c(557mμ log =4·68)



(CLXIII) d(558mμ log =4·68)



(CLXIII) e(570mμ log ε=4·59)



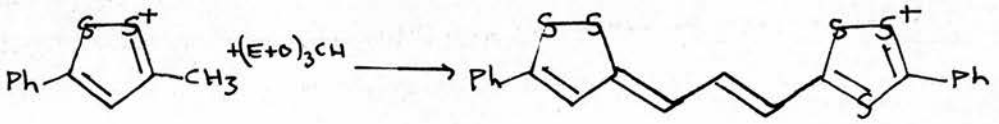
(CLXIII) f.

The last compound (CLXIII f) could not be purified to give a product with a sharp melting point. It was not analysed.

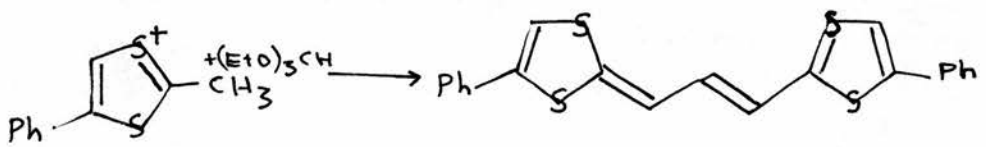
The ultra-violet spectra of these compounds are quite similar. It can be seen that substitution of the hydrogen atom on the central methine carbon by a phenyl group has little effect, if any, on the height, or the position of maxima in the visible region of the spectrum.

Attempts were made to prepare the trimethine cyanine dyes (CLXIV) and (CLXV) by the reaction of 3-methyl-5-phenyl-I,2-dithiolium perchlorate (XXIb) and of 2-methyl-4-phenyl-I,3-dithiolium perchlorate (LIVb) with ethyl orthoformate.

In the case of the I,2-compound, a deep blue dye with a yellow reflex was obtained. This did not give good analytical results, but its deep blue colour indicated that it was substantially the correct product. With the I,3-compound, a deep blue substance was obtained, but analysis showed that it was highly impure, and probably contained a large proportion of the starting material. Both dyes were very difficult to recrystallise.



(XXIb) (CLXIV)



(LIVb) (CLXV)

CONCLUSION.

Following the classification used in the "Object of Research", type(A) reaction seems to hold generally for the reactions of dithiolium salts, except where the attacking species has a high thiophilicity, in which case type(B) reaction occurs.

If type(A) product is suitably constituted, i.e. with electrons easily available for conjugation, the reaction(C) may follow, with possible further reaction of type(E). In the I,2-dithiolium series, compared to the I,3-dithiolium series, type(E) reaction does not occur by the elimination of hydrogen sulphide, with the possible exception of the reaction between I,2-dithiolium salts and ammonia. This is because the intermediate of type(A), after ring-opening of type(C) does not cyclise again, but the S - S group tends to lose sulphur, and the intermediate can now rearrange to the stable thione structure. In the I,3-dithiole series, this loss of a sulphur atom does not occur, and ring closure can occur with loss of hydrogen sulphide.

The reaction of type(B), involving nucleophilic attack at sulphur, probably only occurs with cyanide ion and p-toluenethiolate anion. In this case it is probably followed by type(D) reaction. The open chain compounds then presumably further decompose. The reaction with ammonia is discussed below.

Type(A) reaction products have been obtained from the reactions of 2,4,5-triphenyl-I,3-dithiolium perchlorate with ammonia in dry benzene, from sodium ethoxide, sodium cyanide, and sodium hydroxide in ethanol. They were also obtained from the reaction of 3,5-diphenyl-I,2-dithiolium perchlorate with sodium ethoxide in ethanol.

Type(A) products doubtlessly also occur in the reaction of 3-methylthio--5-phenyl-I,2-dithiolium iodide with morpholine, and of the above salt and its I,3-dithiolium isomer with the anhydrobases of 3-methyl-I,2-dithiolium salts and 2-methyl-I,3-dithiolium salts. In these cases, methanethiolate anion was lost. These reactions can be further classified as type(A)(ii). A hydride ion can also be lost, as in the case of the reaction between 3-unsubstituted-I,2-dithiolium salts and methylaniline.

Type(C) reactions occur with the ethoxy, anilino, and dimethylanilino addition products of 3,5-diphenyl-I,2-dithiolium perchlorate. In each case, cleavage of the dithiole ring occurs by one of the mechanisms outlined in

the discussion above. This type includes the reactions between aniline and methyl aniline with 3-phenyl and 4-phenyl-I,2-dithiolium perchlorates.

Type (E) reaction, involving ring closure of a type C. product, is found in the case of the imino intermediate (CXLIII) forming triphenylthiazole by the elimination of hydrogen sulphide from it. Two other ring closures have been found, which do not involve the elimination of hydrogen sulphide. These are the reactions forming the benzothiapyrylium salt (CXXXII), and the ethoxycarbonyl-4,6-diphenylthiapyran-2-one. (CXXXVII)

Type (G) reaction products were only obtained uncombined where the resulting anhydrobase was stable as in the case of the benzylidenedithioles (LXXI) and (CXIII), although the condensation reactions of 3-methyl-I,2-dithiolium salts and of 2-methyl-I,3-dithiolium salts must have involved the formation of such intermediates. In these cases, however, the anhydrobases would have been stabilised by resonance.

The reactions of 3-methyl-5-phenyl-I,2-dithiolium perchlorate with methyldithiobenzoate, and ethylorthoformate are therefore included in this type.

The self-condensation reactions of 3-methyl-5-phenyl-I,2-dithiolium perchlorate and the cyanine forming reactions of it and its I,3-dithiolium isomer with methylthio dithiolium salts proceed initially by this reaction type (G) However, in these cases, the resulting anhydrobases function as nucleophilic species and type (A) reaction occurs with more dithiolium salt. In the case of the methylthiodithiolium salt, a cyanine dye is formed by loss of methanthiolate anion (Type A.(ii)) and of acid. In the case of the self-condensation reaction, ring opening occurs, (type (C)), with cyclisation to a spiropyran (CLVI) (type (E)).

The reaction of I,2-dithiolium salts with ammonia, as mentioned above, can possibly occur via two different mechanisms. No definite conclusions about this can be reached as a result of the above research, although it would seem likely, in view of the fact that attack by aniline is at a carbon atom (type (A)), that the attack by ammonia must be at a sulphur atom, (type (B)) since the attack at a carbon atom would be expected to produce the iminothione type of structure (CXXVII) by elimination of a sulphur atom.

Type (H) reaction, involving loss of a nuclear proton, was not found.

EXPERIMENTAL PROCEDURES AND RESULTS.

All melting points given, unless otherwise stated, were carried out in a capillary tube in an n-butylphthalate bath, and are uncorrected.

Solutions were dried over anhydrous sodium sulphate, and chromatography was effected on alumina. (Type H., supplied by Peter Spence and Sons Ltd., Widnes.)

Ultraviolet spectra were determined on a Unicam Model S.P. 500 U.V. spectrophotometer and on a Perkin-Elmer model 137 U.V. spectrophotometer.

Infra-red determinations were made on a Perkin-Elmer "Infracord" spectrophotometer.

N.M.R. data were kindly supplied by Perkin-Elmer Ltd.

Analyses were by Dr.Weiler and Dr.Straus of Oxford, and by Dr. Minnis of Andrew H. Baird Ltd.,Edinburgh.

MATERIALS.

Preparations of 1,2-Dithiolium Salts.

Phenylmalondialdehyde.

This compound was prepared[79] from phenylacetic acid. It could not be obtained crystalline as previously reported but the resulting oil obtained from a dried ethereal extract was used in all reactions.

Reaction between phenylmalondialdehyde and hydrogen disulphide.

A dry ether solution (100 ml.) containing crude phenylmalondialdehyde (3g.) was saturated with hydrogen chloride. Hydrogen disulphide (3ml.) was added and the mixture was left three days. No precipitate was obtained.

3-Benzyl-5-phenyl-1,2-dithiolium perchlorate.

Benzoylphenylacetone[51] (8g.) was dissolved in 100 ml. of dry benzene saturated with anhydrous hydrogen chloride. Hydrogen disulphide[76] (6 ml.) was then added. The solution became cloudy and precipitated an oil which began to crystallise after ten minutes. The mixture was left three days, and the product was collected and converted to the perchlorate in acetic acid containing perchloric acid. It was crystallised from acetic acid containing two drops of perchloric acid (70%).

Yield = 9·2g = 74%

$C_{16}H_{13}S_2ClO_4$ requires C = 52·1%, H = 3·53%, S = 17·3%, Cl = 9·62%.

Found C = 51·97%, H = 3·73%, S = 17·41%, Cl = 9·59%.

A solution of the perchlorate in ethanol slowly became orange on standing.

Reaction between nitromalondialdehyde and hydrogen disulphide.

The sodium salt of nitromalondialdehyde[77] (6g., monohydrate) was suspended in 100 ml. of dry benzene and a stream of dry hydrogen chloride was passed through for fifteen minutes. The solution was decanted from solid material, and to it was added 4 ml. of hydrogen disulphide. The colour of the solution changed from reddish to green, and finally to orange. The mixture was left three days, and filtered. The product was soluble only in dimethylformamide but it could not be crystallised. On heating it slowly darkened.

4-Phenyl-1,2-dithiole-3-thione.

The method of Fields[80] was modified by the use of quinoline instead of di-o-tolylguanidine as a basic catalyst.

Yield = 136 g. from 120 g. of cumene = 65%.

4-Phenyl-1,2-dithiolium perchlorate.

The method of Klingsberg[7] was modified in the following way. The calculated quantity of hydrogen peroxide (30%) was added without cooling to a solution of 4-phenyl-1,2-dithiole-3-thione in acetic acid. After standing one hour, the solution was treated with perchloric acid. Dilution with ether precipitated the perchlorate.

M.P. = 210°C.

Yield = 1·76g. from 2·1g. of thione = 63·5%.

3-Phenyl-1,2-dithiolium perchlorate.

The method of Klingsberg[7] was modified as described above for the 4-phenyl compound.

Yield = 1·51g. from 2·1g. of thione = 55%.

1,2-Dithiolium perchlorate.

1,2-Dithiole-3-thione[52] (0·4g) was dissolved in glacial acetic acid (10 ml.) at room temperature and 30% hydrogen peroxide (1·0ml.) added, keeping the temperature below 30°C. After 20 minutes the solution was filtered, and 70% perchloric acid (0·5 ml.) was added. Dilution with ether precipitated the crude perchlorate (0·33g.). It was recrystallised from glacial acetic acid containing perchloric acid. The salt had no definite melting point, but exploded violently on combustion.

$C_3H_3S_2ClO_4$ requires C = 17·8%, H = 1·49%, S = 31·6%, Cl = 17·5%.

Found C = 17·74%, H = 1·46%, S = 32·4%, Cl = 18·08%.

3-Chloro-5-phenyl-1,2-dithiolium perchlorate.

Chlorine was passed during ten minutes into a suspension of 5-phenyl-1,2-dithiole-3-thione in glacial acetic acid (10 ml.). The pale yellow solution was filtered, and diluted with an equal volume of ether. Oily crystals were deposited.

The supernatant liquid was rejected, and the crystals were converted in acetic acid to the perchlorate which was crystallised from acetic acid containing perchloric acid.

Yield of pale yellow needles = I·Ig. = 37%.

$C_9H_6S_2ClO_4$ requires C = 34·6%, H = I·92%, S = 20·4%, Cl = 22·3%.

Found C = 34·67%, H = 2·I3%, S = I8·2%, Cl = 24·3%.

Preparations of 1,3-Dithiolium Salts.

1,3-Dithiole-2-thione.

A solution of 2-oxoethyl-ethylxanthate[11] (9g.) in tetralin (100ml.) was boiled with phosphorus pentasulphide (18g.) for twenty minutes. To the solution was added a saturated methanolic solution of mercuric chloride (20 ml.). The mercuric chloride complex was filtered off, and decomposed by treatment with aqueous sodium sulphide solution. The resulting suspension was then extracted, twice with ether, and, after filtration, the solid residue (mainly MgS) was extracted with hot acetone (4 x 20 ml.). These extracts were united, evaporated and chromatographed on alumina in benzene. The first yellow band was collected and on evaporation the eluate yielded a yellow oil, which crystallised from light petroleum (40-60°) as yellow needles (M.P. = 49-50°C.)

Yield = 1·32g. = 18%.

1,3-Dithiolium perchlorate.

1,3-Dithiole-2-thione (0·47g.) dissolved in glacial acetic acid (8ml.) was treated with 30% hydrogen peroxide solution (1·2 ml.), keeping the temperature below 30°. After one hour the solution was decanted from an oil which had formed, and diluted with ether. The mixture of oil and water that precipitated was dissolved in hot methanol, to which 2 drops of 70% perchloric acid were added. Dilution with ether precipitated the perchlorate, which was crystallised from glacial acetic acid containing perchloric acid.

Yield of white needles = 0·14g = 21%.

$C_3H_3S_2ClO_4$ requires C = 17·8%, H = 1·49%, S = 31·6%, Cl = 17·5%.

Found C = 18·27%, H = 1·51%, S = 31·6%, Cl = 17·15%

4-Phenyl-1,3-dithiolium salts.

4-Phenyl-1,3-dithiole-2-thione[11] (0·21g.) dissolved in 10 ml of a mixture of acetone and acetic acid (50/50) was treated with 0·34 ml. of 30% hydrogen peroxide solution. The solution was stirred for one minute and set aside for one hour. The solution was then decanted into 20 ml. ether, and the precipitate collected. It was treated with charcoal in acetic acid, and recrystallised from the same medium containing 1 drop of concentrated sulphuric acid to give 4-phenyl-1,3-dithiolium hydrogen sulphate.

Yield = 0·09g. = 33%. M.P. = 188°C.
(turned brown, solidified, and remelted at 232°C.)

$C_9H_8S_3O_4$ requires C = 39·1%, H = 2·9%, S = 34·8%.

Found C = 39·16%, H = 3·12%, S = 35·15%.

The sulphate was converted to the perchlorate in glacial acetic acid containing perchloric acid. M.P. = 161°C.

$C_9H_7S_2ClO_4$ requires C = 38·7%, H = 2·51%, S = 23·0%, Cl = 12·7%.

Found C = 38·8%, H = 2·68%, S = 23·15%, Cl = 12·55%.

Phenyldithioacetic acid.

The product[81] was obtained as a solution of its sodium salt after being purified by an extraction technique.[83]

Phenacyl phenyl(dithioacetate).

The sodium salt of the dithioacid was freed of any traces of free alkali by the dropwise addition of concentrated acid until the free dithioacid began to precipitate. The solution (35 ml, 1·25N) was added slowly with shaking to a solution of phenacyl bromide (7·2g.) in ethanol (200ml.) and more ethanol added, if necessary, to give a clear solution. The mixture was kept at 0°C for one hour, then water added until cloudy. After leaving fifteen hours, the crystalline precipitate was filtered off, and dried. It was crystallised from light petroleum as fibrous yellow needles. (M.P. = 48°C)

Yield = 5·6g = 52%.

$C_{16}H_{14}S_2O$ requires C = 66·75%, H = 4·89%, S = 22·37%.

Found C = 67·13%, H = 4·93%, S = 22·30%.

2-Benzyl-4-phenyl-1,3-dithiolium perchlorate.

S-Phenacyl-phenyl (dithioacetate) (1g.) was dissolved in ether (50 ml.). The solution was saturated with hydrogen sulphide and 3·5 ml. of boron trifluoride ether complex added. After one hour an orange oil was precipitated which soon crystallised. After one day the ether was decanted off, and the precipitate

dissolved in hot acetic acid containing perchloric acid (I ml, 70%). The perchlorate precipitated in pink plates and was recrystallised from glacial acetic acid. (M.P. = 113°C, Lit[37] 113°C).

Yield = 1·05g = 74%.

The perchlorate was shaken with dilute sodium carbonate solution to yield 2-benzylidene-4-phenyl-1,3-dithiole (M.P. = 204°C) from acetic acid or toluene. (Lit[37] M.P. = 205-207°C.)

λ max=354 mμ (log ε = 4·34) in dioxan. (Lit[37] 354 (4·33) in tetrahydrofuran.)

3,4-Diphenyl-thiophen-2-thiol.

Sodium phenyl (dithioacetate) (2·5g), in water (12·5 ml.) was slowly added to a boiling solution of phenacyl bromide (2·2g) in ethanol (50 ml). The mixture was boiled for ten minutes, poured into water, and extracted with ether. The extract was washed with alkali (NaOH) and water, and dried. Evaporation yielded a red oil which was chromatographed on alumina. Evaporation of the eluate from the first band yielded a yellow oil which crystallised from light petroleum (40-60°) with cooling in a solid carbon-dioxide / acetone mixture as a pale yellow powder (M.P. = 62°C).

Yield = 2·03g.

$C_{16}H_{12}S_2$ requires C = 71·9%, H = 4·5%, S = 23·8%.

Found C = 72·22%, H = 4·19%, S = 23·45%.

The eluates from other bands yielded only traces of products.

Desulphurisation of 3,4-diphenyl-thiophen-2-thiol.

3,4-Diphenylthiophen-2-thiol (0·2g) dissolved in boiling ethanol was treated with a large excess of Raney nickel under reflux for one hour. The nickel was filtered off, and the solution diluted with water. Colourless crystals of meso-2,3-diphenylbutane were deposited after two days at room temperature. (M.P. = 125°C.) (Lit[78] M.P. = 126-7°C.)

4,5-Dicyano-1,3-dithiole-2-thione.

The disodium salt of 2,3-dimercaptomaleinitrile[85] (4g) dissolved in methanol (80 ml.) was treated with thiocarbonyl chloride[84] (2·4g). After

standing for one hour the mixture was diluted with water (200 ml). The crystalline precipitate was filtered off, and recrystallised from methanol (M.P. = 115°C.)

Yield = 2·6g. = 65%.

2-Thio-1,3-dithiole-4,5-dicarboxylic acid.

4,5-Dicyano-1,3-dithiole-2-thione (1g.) was boiled under reflux for 30 minutes with 50% sulphuric acid (60 ml.) and acetic acid (5 ml.). After treatment twice with charcoal, the solution deposited the acid as pale yellow needles (M.P. = 173°C) on cooling.

Yield = 0·4g = 33%.

$C_5H_2S_3O_4$ requires C = 27·1%, H = 2·44%, S = 43·3%.

Found C = 25·02%, H = 2·44%, S = 43·3%.

New Sample C = 27·15%, H = 1·51%, S = 51·0%.

Attempted oxidation of 2-thio-1,3-dithiole-4,5-dicarboxylic acid.

The thione (0·44g) dissolved in acetone (5 ml) and acetic acid (2 ml) was treated with 0·68 ml. of 30% hydrogen peroxide, keeping the temperature below 30°C. No ether insoluble fraction could be isolated.

Attempted synthesis of 4,5-dicarboxy-2-methylthio-1,3-dithiolium iodide.

The thione (0·2g) was dissolved in 10 ml of N-butyl acetate and methyl iodide (1 ml.) was added. No precipitate was obtained on boiling under reflux.

REACTIONS OF I,2-DITHIOLIUM SALTS WITHOUT REPLACEABLE SUBSTITUENTS.

I,2-Dithiolium Perchlorate.

Reaction with ammonium acetate. To the perchlorate (0·25g.) dissolved in acetic acid (20 ml) was added a saturated solution of ammonium acetate in acetic acid (20 ml). On heating, hydrogen sulphide was evolved, and the solution became yellow. Addition of a saturated solution of mercuric chloride in acetic acid (5 ml) produced a slight yellow precipitate which had an indefinite melting point.

Reaction with diethylsodiomalonate. To a boiling solution of I,2-dithiolium perchlorate (0·4g.) in ethanol (10 ml) was added a solution of diethylmalonate (0·320g.) and sodium (0·046g.) in ethanol (10ml). The solution was boiled briefly, and partitioned between ether and water. The dried ether extract on chromatography on alumina in benzene yielded a few mg. of I,2-dithiole-3-thione.

4-Phenyl-I,2-dithiolium perchlorate.

Reaction with ammonia.

a). In acetic acid. 4-Phenyl-I,2-dithiolium perchlorate (I·5g.) in boiling acetic acid (50 ml) was treated with 10 ml of a saturated solution of ammonium acetate in acetic acid. The mixture was boiled for ten minutes, filtered, and evaporated under reduced pressure. The oily residue was partitioned between ether and water, the dried ether layer was evaporated, andthe residue was dissolved in acetic acid containing perchloric acid. Addition of light petroleum (40-60°) precipitated the perchlorate of the base. (M.P. = 152-3°C.)

Yield = 0·61g.

$C_9H_8SNClO_4$ requires C = 41·3%, H = 3·06%, S=12·24%, N = 5·36%, Cl = 13·6%.

Found C = 39·72%, H = 3·77%, S = 12·34%, N = 5·29%, Cl = 13·80%.

C = 38·74%, H = 3·07%.

The perchlorate was reconverted to the free base by shaking with N-sodium hydroxide solution and ether. The dried ether layer on evaporation yielded 4-phenyl-iso-thiazole, M.P. = 36°C. (from light petroleum (40-60°)).

Yield = 0·23g = 27%.

C_9H_7SN requires C = 67·1%, H = 4·34%, S = 19·9%, N = 8·69%.

Found C = 66·74%, H = 4·07%, S = 20·02%, N = 8·54%.

b). In Benzene. A stream of dry ammonia was passed through a suspension of 4-phenyl-I,2-dithiolium perchlorate (2g.) in boiling benzene (75 ml) for five minutes. The solution was filtered, and evaporated to give an orange material (bis-(4-phenyl-I,2-dithiol-3-yl)sulphide) which was washed with ether, and crystallised from benzene. (M.P. = 152°C.)

Yield = 0·7g = 60% (on the basis of the scheme mentioned).

For $C_{18}H_{14}S_5$ C = 55·3%, H = 3·59%, S = 41·05%,.

Found C = 55·35%, H = 4·03%, S = 40·70%.

The ether washings were evaporated to give 0·2g. of a pasty solid. This was crystallised from light petroleum (40-60) to give 0·Ig. of 4-phenylisothiazole.

Reaction of bis-(4-phenyl-I,2-dithiol-3-yl)sulphide with perchloric acid.

0·Ig. of the sulphide was dissolved in 5 ml. of acetic acid and 0·5 ml of perchloric acid was added. The solution , on being boiled briefly, evolved hydrogen sulphide and on cooling it deposited 4-phenyl-I,2-dithiolium perchlorate.

Reaction of 4-phenyl-I,2-dithiolium perchlorate with aniline to form cis-phenylmalondialdehydedianil perchlorate.

4-Phenyl-I,2-dithiolium perchlorate (0·4g.) was heated in a mixture of 3 ml. of aniline and 3 ml. of benzene for five minutes. The solution was left to cool and the precipitate was collected and crystallised from alcohol to give yellow needles of a perchlorate (M.P. = 204°C.)

Yield = 0·42g. = 78%.

$C_{21}H_{18}N_2ClO_4$ requires C = 63·8%, H = 4·52%, N = 7·04%, Cl = 8·91%.

Found C = 60·95%, H = 4·80%, N = 7·43%, Cl = 9·44%.

C = 61·58%, H = 4·87%, N = 7·58%, Cl = 9·36%.

Cis-phenylmalondialdehydedianil.

The perchlorate (0·2g.) was shaken in acetone with 10% aqueous sodium hydroxide solution and water was added to precipitate the free base. The latter, after crystallisation from alcohol, was shown to be cis-phenylmalondialdehydedianil by comparison of its infrared spectrum with that of an authentic specimen and by mixed m.p. determination. (M.P. = 123·5°C).

Yield = 0·14g. = 93·5%.

$C_{21}H_{17}N_2$ requires C = 84·8%, H = 5·73%, N = 9·45%.

Found C = 83·18%, H = 5·88%, N = 9·85%.

C = 84·07%, H = 6·20%, N = 9·88%.

Cis and trans-phenylmalondialdehydedianils.

Aniline (1 ml.) was added to an ether solution containing 0·5g. of phenylmalondialdehyde. The mixture was refluxed for three hours, and left to stand for one week. The precipitate was filtered off, and recrystallised from ethanol (M.P. = 138°C.) (Lit.[86] M.P. = 138°C).

Yield = 0·18g. of trans-phenylmalondialdehydedianil.

The filtrate was evaporated to yield a yellow product, which was crystallised from ethanol (M.P. = 123·5°C.)

Yield = 0·21g. of cis-phenylmalondialdehydedianil.

The stereochemical configurations of these products were assigned on the basis of their NMR spectra as described in the Discussion.

Phenylmalondialdehydedi-(p-methyl)anil.

p-Toluidine (1g.) was dissolved in 1 ml. of benzene, 1g. of 4-phenyl-1,2-dithiolium perchlorate added and the mixture was boiled under reflux for five minutes. The mixture was cooled and the precipitate was filtered off and recrystallised from ethanol (M.P. = 237°C.)

Yield = 0·79g. = 51 2%.

$C_{23}H_{23}N_2ClO_4$ requires C = 64·7%, H = 5·38%, N = 6·55%, Cl = 8·22%.

Found C = 61·85%, H = 5·58%, N = 6·36%, Cl = 8·08%.

3-(p-Methylaminophenyl)-4-phenyl-1,2-dithiolium perchlorate.

3-Phenyl-1,2-dithiolium perchlorate (0·4g.) was heated with methylaniline (1·0ml) for ten minutes. The violet tar produced on cooling could not be crystallised.

Reactions with other nucleophilic reagents.

Reactions with sodium ethoxide, sodium cyanide, sodium hydrogen sulphide, diethyl sodiomalonate, and phenyl magnesium bromide.

The perchlorate (2·7g.) was treated in the appropriate solvent with the calculated quantity (0·01 g. moles) of the reagent. The mixtures were boiled and evaporated to produce oils. The only identifiable product, isolated after chromatography of the oils on alumina in benzene, was 4-phenyl-1,2-dithiole-3-thione.

3-Phenyl- and 3,5-Diphenyl-1,2-dithiolium perchlorates.

Reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with aniline yielding 1-anilino-1,3-diphenylprop-1-ene-3-thione.

Aniline (0·5g.) was added to 0·5g. of 3,5-diphenyl-1,2-dithiolium perchlorate suspended in ethanol (10 ml) and the mixture was boiled under reflux until homogeneous, and left to cool. The product which separated was fractionally crystallised from ethanol to yield the thione (M.P. = 158°C) and a trace of sulphur. The identity of the thione was established by comparison (infrared spectrum and mixed M.P.) with an authentic specimen prepared as described below.

Yield = 0·31g. = 67%.

$C_{21}H_{17}NS$ requires C = 80·1%, H = 5·4%, N = 4·45%, S = 10·9%.

Found C = 80·48%, H = 5·12%, N = 4·1%, S = 10·8%.

Sulphurisation of 1-anilino-1,3-diphenyl-prop-1-ene-3-one.

1-Anilino-1,3-diphenyl-prop-1-ene-3-one[87] (1g.) was boiled with 2·0g. of phosphorus pentasulphide in 10 ml. of carbon disulphide for four hours. The mixture was filtered, and the carbon disulphide was washed with water.

Evaporation produced a red oil, which was crystallised from ethanol to give red plates (M.P. = 158°C.)

Yield of I-anilino-I,3-diphenyl-prop-I-ene-3-thione = 0·23g. = 19%.

I-Anilino-3-phenylprop-I-ene-3-thione.

3-Phenyl-I,2-dithiolium perchlorate(Ig.) suspended in ethanol (5 ml.) was treated with aniline (I ml). The mixture was gently warmed until homogeneous. On cooling it deposited the thione (M.P. = 105·5°C from methanol).

Yield = 0·2g. = 23%.

$C_{15}H_{13}NS$ requires C = 75·2%, H = 5·43%, N = 5·84%, S = 13·4%.

Found C = 75·43%, H = 5·01%, N = 5·6%, S = 13·6%.

I-Methylanilino-3-phenylprop-I-ene-3-thione.

3-Phenyl-I,2-dithiolium perchlorate (0·5g.) was triturated in methanol (5 ml) with methylaniline. (0·5 ml) for ten minutes. The mixture was cooled and the brown crystalline precipitate which formed was washed with light petroleum (B.P. = 40-60°C) and purified by dissolving in benzene, filtering, and precipitating by dilution with light petroleum (M.P. = 93°C.)

Yield = 0·16g. = 35%.

$C_{16}H_{15}NS$ requires C = 75·7%, H = 5·92%, N = 5·53%, S = 12·64%.

Found C = 75·55%, H = 5·77%, N = 5·50%, S = 12·60%.

Reaction between N-Methylaniline and 3,5-diphenyl-I,2-dithiolium perchlorate

The perchlorate (0·36g.) was heated under reflux with N-methylaniline (1·5 ml). A dark violet oil was obtained which could not be crystallised.

3-(p-Methylaminophenyl)-3-phenyl-I,2-dithiolium perchlorate.

3-Phenyl-I,2-dithiolium perchlorate (0·4g.) was heated with 1·0 ml. of methylaniline for ten minutes. The violet dye produced on cooling was extracted with ether, then triturated with 3 ml. of acetone. The dark green product was collected and crystallised from glacial acetic acid (M.P. = 208 -9°C).

Yield = 0·25g. = 45%.

$C_{16}H_{14}N_2S_2ClO_4$ requires C = 50·1%, H = 3·66%, N = 3·65%, S = 16·7%
Cl = 9·3%.

Found C = 50·31%, H = 3·83%, N = 3·43%, S = 14·5%,
Cl = 9·0%.

Reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with dimethylaniline.

The perchlorate (0·36g.) was heated under reflux with dimethylaniline (1·5 ml) for five minutes. The cooled mixture was extracted with ether (3x5 ml) and the residual oil was dissolved in 1 ml. of hot methanol. To the hot solution were added three drops of perchloric acid and the precipitate obtained on cooling was crystallised from ethanol containing perchloric acid. (M.P. = 236-8°C.)

Yield = 0·23g. = 51%.

$C_{23}H_{20}N_2S_2ClO_4$ requires C = 62·4%, H = 4·52%, N = 3·16%, S = 7·13%, Cl = 8·02%.
Found C = 61·9%, H = 4·71%, N = 2·96%, S = 6·7%, Cl = 8·5%.

This analysis corresponds reasonably well to that required for 7-dimethylamino-2,4-diphenylbenzothiopyrylium perchlorate.

Reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with sodium ethoxide.

3,5-Diphenyl-1,2-dithiolium perchlorate (1g.) was added to a boiling solution of sodium ethoxide (70 mg. of sodium) in 10 ml. of ethanol, and boiling was continued until the compound dissolved. The orange solution was evaporated and the residue extracted with light petroleum (40-60°). Evaporation of the extract under reduced pressure yielded 3-ethoxy-3,5-diphenyl-1,2-dithiole which was recrystallised from light petroleum (40-60°) with seeding (M.P. = 68-69°).

Yield = 0·51g. = 60%.

$C_{17}H_{16}S_2O$ requires C = 68·0%, H = 5·33%, S = 21·33%.
Found C = 67·62%, H = 5·09%, S = 20·80%.

Decomposition of 3,5-diphenyl-3-ethoxy-1,2-dithiole.

A solution of 0·5g. of the ethyl ether in benzene was added to a short length of alumina in a column. When the red colour had reached its greatest

intensity, the column was quickly stripped with acetone. Evaporation of the eluate and fractional crystallisation from light petroleum (B.P. = 40-60°C) yielded 0·14g. of red crystals (M.P. = 73°C.)

Required for $C_{17}H_{16}SO$	C = 76·3%, H = 5·96%, S = 11·92%.
Found	C = 72·06%, H = 4·51%, S = 15·72%.
	C = 72·23%, H = 4·77%, S = 15·63%.
New Sample	C = 74·83%, H = 5·32%, S = 10·6%.

4,6-Diphenyl-3-ethoxycarbonyl-thiopyran-2-one.

A solution of diethyl-sodiomalonate prepared from 0·23g. of diethyl malonate and 0·03g. of sodium in 10 ml. of dry ethanol was evaporated to dryness and the residue was suspended in 50 ml. of ether. To the suspension was added 0·5g. of 3,5-diphenyl-1,2-dithiolium perchlorate and the mixture was heated under reflux (water-bath) for 1½ hours. After filtration, the solution was evaporated under reduced pressure to yield a brown oil which crystallised when treated with light petroleum (B.P. = 40-60°C) and was recrystallised from the same solvent. (M.P. = 77°C.)

Yield = 0·35g. = 74%.

Required for $C_{20}H_{16}SO$	C = 71·43%, H = 5·13%, S=9·52%.
	C = 71·51%, H = 4·98%, S = 9·42%.

4,6-Diphenylthiopyran-2-one.

4,6-Diphenyl-3-ethoxycarbonyl-2-one (0·55g.) was boiled under reflux for twenty-five minutes in 20 ml. of 25% sulphuric acid in acetic acid. The cooled solution was diluted with cold water and extracted with ether (2 x 25 ml). The dried extracts, on evaporation, yielded a pale orange product which was crystallised from ethanol (M.P. = 97-98°C)

Yield 0·41g. = 93%.

Required for $C_{17}H_{12}SO$	C = 77·2%, H = 5·32%, S = 12·15%.
Found	C = 76·68%, H = 4·93%, S = 12·35%.

4,6-Diphenylthiopyran-2-thione.

4,6-Diphenyl-thiopyran-2-one (0·25g.) was boiled under reflux in carbon

disulphide (25 ml.) with phosphorus pentasulphide (1g.) for five hours. The solution was filtered, and the residue extracted with benzene. The two united solutions on washing (sodium carbonate, water) and evaporation produced a dark red oil, which was crystallised from alcohol. (M.P. = 119°C).

Yield = 0·18g. = 68%.

$C_{17}H_{12}S_2$ requires C = 72·8%, H = 4·28%, S = 22·8%.

Found C = 72·78%, H = 4·25%, S = 22·54%.

Triphenylthiopyrylium perchlorate.

To 4,6-diphenylthiapyran-2-one (0·05g.) dissolved in ether (5 ml.) was added an excess of phenylmagnesium bromide in ether. The mixture was left for four hours, then diluted with dilute hydrochloric acid. To the dried ether layer was added 0·5 ml of perchloric acid and the resulting precipitate was collected and crystallised from acetic acid containing perchloric acid (M.P. = 209-210°C) (Lit.[60] gives 2,4,6-triphenylthiopyrylium perchlorate (M.P.= 210-211°C.))

Yield = 10 mg = 12·4%.

Reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with sodium cyanide in ethanol.

The perchlorate (0·7g.) was boiled in ethanol (30 ml.) with sodium cyanide (0·1g.). The solution became green then brown. Evaporation and extraction of the residue with ether yielded a brown oil, which was resolved by chromatography in benzene on alumina into three oils, yellow, red, and orange. These could not be crystallised, but infra-red spectroscopy showed the presence of nitrile groups in both the red and orange oils.

Reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with sodium-p-toluenethiolate.

3,5-Diphenyl-1,2-dithiolium perchlorate (1·7g.) was added to a solution of 0·62g. of p-toluenethiol and 0·11g. of sodium in 25 ml. ethanol. The mixture almost immediately turned brown. The oil obtained on evaporation could not be resolved by chromatography.

Reaction between 3,5-diphenyl-I,2-dithiolium perchlorate and sodiocyclopentadiene.

Redistilled cyclopentadiene (0·5 ml) was added to sodium powder[88] (0·Ig.) suspended in tetrahydrofuran (I5 ml.) under a stream of nitrogen. After one hour the perchlorate was added in small portions. The mixture became violet, and after fifteen minutes the colour changed to deep red. The solvent was removed, and the residue chromatographed on alumina in benzene. The only product obtained was an oil with a blue fluorescence which could not be crystallised.

Reaction of 2,4,5-triphenyl-I,3-dithiolium perchlorate with nucleophilic reagents.

I. Sodium ethoxide.

To a solution of the perchlorate (2·I5g.) in ethanol (I50 ml) was added a solution of sodium ethoxide (0·II5g. sodium) in 50 ml. of ethanol. The mixture was boiled five minutes and the solvent was evaporated under reduced pressure. The residue was extracted with ether and the extract was evaporated to yield 2-ethoxy-2,4,5-triphenyl-I,3-dithiole which was crystallised from ethanol. (M.P. = II3°C.)

Yield = I·Ig. = 58·5%.

Required for $C_{23}H_{20}S_2O$ C = 73·4%, H = 5·32%, S = I7·I%.

Found C = 73·I6%, H = 5·54%, S = I6·98%.

Sodium cyanide.

To a hot solution of the perchlorate (2·I5g.) in ethanol (I00 ml.) was added a hot solution of sodium cyanide (0·245g.) in ethanol (30 ml.). The mixture was boiled for five minutes and evaporated. The residue was extracted with ether, which on evaporation furnished 2-ethoxy-2,4,5-triphenyl-I,3-dithiole. (Yield = 0·52g. = 29%.) The residue was further extracted with benzene and the extract was evaporated to give 2-cyano-2,4,5-triphenyl-I,3-dithiole as a yellow powder which crystallised from benzene. (M.P. = I92-3°C, sublimed above I30°).

Yield = 0·52g. = 29%.

Required for $C_{22}H_{18}S_2N$ C = 73·9%, H = 4·2%, S = I7·95%, N = 3·93%.

Found C = 73·94%, H = 4·II%, S = I6·50%, N = 3·92%.

S = I5·70%, I4·85%.

Sodium hydroxide.

To a hot solution of 0·2g. of the perchlorate in ethanol (20 ml) was added a slight excess of sodium hydroxide in ethanol (0·025g. in 5 ml). The mixture was shaken and left for two days. The product which separated was recrystallised from ethanol. The yield of 2-ethoxytriphenyl-I,3-dithiole was = 0·I05g. = 50%.

II. Ammonia.

a). In benzene. The pure dry perchlorate (2·2g.) was suspended in 50 ml. of sodium-dried benzene, and dry ammonia gas (by quicklime) was passed through for ten minutes. The resulting yellow solution was decanted from a finely divided solid and evaporated under reduced pressure to give a pale orange solid. Recrystallisation from benzene/light petroleum I/I afforded 2-amino-2,4,5-triphenyl-I,3-dithiole as colourless needles. (M.P. = II2-II3°C.)

Yield = I·Ig. = 63·5%.

Required for $C_{21}H_{20}S_2N$ C = 72·6%, H = 5·76%, N = 4·04%, S = I8·5%.

Found C = 72·78%, H = 4·50%, N = 4·I6%, S = I8·29%.

b). In ethanol. The perchlorate (2·2g.) in boiling ethanol (200 ml.) was treated with a stream of ammonia gas for ten minutes. The solution was evaporated to yield a yellow oil, which was chromatographed on alumina. Elution with benzene produced successively sulphur (3 mg.), a yellow oil, and desoxybenzoin (30 mg.), identical in m.p. and infrared spectrum with an authentic specimen.

Further elution with ether produced 25 mg. of a pale yellow solid, identical with thiobenzamide by infrared spectroscopy and mixed melting-point.

The yellow oil could not be crystallised. When dissolved in alcohol and treated with perchloric acid it regenerated the original perchlorate.

c). In acetic acid. The perchlorate (2·2g.) in 60 ml. of boiling acetic acid was treated with I0 ml. of a saturated solution of ammonium acetate in acetic acid. The mixture evolved hydrogen sulphide and was boiled for a further ten minutes. The acetic acid solution was evaporated in vacuo, and the residue was extracted twice with benzene. The benzene was evaporated to give an ether soluble oil, and an insoluble solid.

The solid was recrystallised from dimethyl-formamide to give pale yellow prisms of 2,4,5-triphenyl-I,3-dithiole (M.P. = 242°C).

Yield = 0·42g.

$C_{21}H_{16}S_2$ requires C = 75·7%, H = 4·82%, S = I9·29%.

Found C = 75·26%, H = 4·59%, S = I9·66%.

The oil could not be resolved by chromatography. In alcohol it yielded, on treatment with perchloric acid, a mixture of 2,4,5-triphenyl-I,3-dithiolium perchlorate and 2,4,5-triphenyl-thiazolium perchlorate.

This mixture could only be partially resolved by fractional crystallisation (from acetic acid). The melting points of the components were rather indefinite, but the least soluble perchlorate had an infrared spectrum identical to 2,4,5-triphenyl-I,3-dithiolium perchlorate, and the more soluble had an infrared spectrum identical to a sample of triphenylthiazolium perchlorate prepared from triphenylthiazole and perchloric acid.

Preparation of 2,4,5-triphenyl-I,3-dithiolium perchlorate from 2,4,5-triphenyl-I,3-dithiole.

The I,3-dithiole (0·Ig.) was boiled under reflux in acetic acid with a slight excess of triphenylmethyl perchlorate[89] for two minutes. The mixture was filtered, and diluted with ether, and the precipitate was recrystallised from acetic acid. It was shown to be identical with 2,4,5-triphenyl-I,3-dithiolium perchlorate by mixed melting point and infrared spectrum.

Decomposition of 2-amino-2,4,5-triphenyl-I,3-dithiole.

The amine (I g.) was boiled for 30 minutes in 50 ml. of ethanol. Hydrogen sulphide was evolved gradually and a pale yellow precipitate was formed. This was filtered off to yield 0·2g. of triphenyl-I,3-dithiole and a little sulphur. The ethanol was evaporated and the residue was dissolved in light petroleum (B.P. = 40-60°C) (I0 ml) which, on standing, deposited thiobenzamide. Further evaporation of the solution afforded first triphenylthiazole (0·45g.) which was recrystallised from ethanol , and then desoxybenzoin, crystallised from light petroleum (B.P. = 40-60°C).

All these products were identified by comparison of their infrared spectra with those of authentic specimens.

Reaction of 2,4,5-triphenyl-I,3-dithiolium perchlorate with sodium hydrogen sulphide.

The perchlorate (0·I5g.) was treated with a slight excess of sodium

hydrogen sulphide in ethanol (10 ml), and the mixture was boiled briefly. On cooling, it deposited 2,4,5-triphenyl-1,3-dithiole.

Yield = 0·1g. = 88%.

Reaction of 2,4,5-triphenyl-1,3-dithiolium perchlorate with phenylmagnesium bromide.

The Grignard reagent prepared from magnesium (0·12g.) and bromobenzene (0·89g.) in ether (10 ml.) was added to the finely powdered perchlorate (2·2g.) in ether (100 ml). The mixture was stirred vigorously for one day, 1 ml. of water was added, and the ether layer was separated. Evaporation of the ether and chromatography on alumina yielded a yellow oil mixed with triphenyl-1,3-dithiole (5 mg.). The oil, when treated with perchloric acid, yielded the original perchlorate.

REACTIONS OF 1,2-DITHIOLIUM SALTS CONTAINING REPLACEABLE SUBSTITUENTS.

3-Morpholino-5-phenyl-1,2-dithiolium perchlorate.

3-Methylthio-5-phenyl-1,2-dithiolium iodide (1g.) was treated with morpholine (1 ml) in ethanol (10 ml). The mixture was boiled briefly and after cooling, the product which crystallised was converted to the perchlorate in glacial acetic acid : acetone (2:1). It was recrystallised from the same solvent. (M.P. = 185-6°C.)

Yield = 0·62g. = 60%.

Required for $C_{13}H_{14}NSClO_5$ C = 43·0%, H = 3·97%, N = 3·97%, S = 18·17%, Cl = 10·1%.

Found C = 42·59%, H = 3·90%, N = 3·8%, S = 18·1%. Cl = 10·4%.

Reaction of 5-phenyl-1,2-dithiole-3-thione with phenacyl bromide.

Phenacyl bromide (1g.) was added to 5-phenyl-1,2-dithiole-3-thione (1·05g.) in warm nitromethane (30 ml). The mixture was left for one day, and the yellow product was collected. Yield of crude material - 1·5g. (M.P. decomp = 152°C). The product was converted to the perchlorate in acetic acid/perchloric acid (10/1) and recrystallised from the same medium. (M.P. = 181°C decomp.).

Yield = 1·45g. = 68%.

$C_{17}H_{13}S_3ClO_5$ requires C = 47·6%, H = 3·04%, S = 22·4%, Cl = 8·3%.

Found C = 46·78%, H = 3·44%, S = 21·9%, Cl = 8·7%.

Reaction of 5-phenyl-3-phenacylthio-1,2-dithiolium perchlorate with triethylamine.

The perchlorate (0·43g.) suspended in 10 ml. of glacial acetic acid, was treated with triethylamine (1 ml). The mixture was shaken for ten minutes, diluted with water (10 ml), and the resulting precipitate was filtered and dried. It could not be satisfactorily recrystallised from any solvent, so it was purified by chromatography on alumina in benzene. The red band was collected and gave a red oil which solidified under light petroleum (40-60°)/

/ethanol,(4/I) to a bright red powder. The product showed no carbonyl absorption in the infra-red. (M.P. = 128°C.)

$C_{17}H_{12}S_2O$ requires C = 68·9%, H = 4·06%, S = 21·6%.
Found C = 62·1%, H = 3·38%, S = 26·8%.
$C_{17}H_{12}S_3O$ requires C = 62·1%, H = 3·65%, S = 29·3%.

Reaction of diazoacetophenone with 5-phenyl-I,2-dithiole-3-thione.

5-Phenyl-I,2-dithiole-3-thione (0·5g.) was gently fused with diazoacetophenone[90] (0·3g.) until a vigorous reaction ensued. The mixture was chromatographed on alumina in benzene. Two bands were eluted; one gave unreacted thione, while the other afforded 3-phenacylidene-5-phenyl-I,2-dithiole.

Yield = 0·045g. = 6%.

Benzoylacetic acid.

The acid was prepared by hydrolysis of benzoylacetic ester[91], but the procedure was modified in that the alkaline solution was extracted once with ether to remove oily material. The cooled solution was acidified with dilute sulphuric acid to yield the acid which was collected, washed well with water, and dried. This crude acid was used for all reactions involving the use of benzoylacetic acid.

3-Phenacylidene-5-phenyl-I,2-dithiole.

To a suspension of sodium benzoylacetate in alcohol (prepared from sodium ethoxide (0·07g.Na) and benzoylacetic acid (0·5g.)in ethanol (50 ml.)) was added, with shaking, 3-methylthio-5-phenyl-I,2-dithiolium iodide (Ig.). The mixture was gently heated until homogeneous, and evaporated under reduced pressure. Chromatography on alumina in benzene afforded first a pale pink band, which produced white crystals (from ethanol, M.P. = 204°C).

Found C = 69·58%, H = 3·52%, S = 13·8%.

Two orange bands were eluted next. The first afforded 0·3g. of 5-phenyl-I,2-dithiole-3-thione, and the second 3-phenacylidene-5-phenyl-I,2-dithiole, which was crystallised from alcohol. (M.P. = 93°C.)

Yield = 0·38g. = 46%.

$C_{17}H_{12}S_2O$ requires C = 68·9%, H = 4·06%, S = 21·6%.

Found C = 69·1%, H = 3·9%, S = 21·7%.

Sulphurisation of 3-phenacylidene-5-phenyl-I,2-dithiole.

The phenacylidene compound (0·3g.) was treated in boiling benzene (20 ml.) with phosphorus pentasulphide (I·0g.) for one hour. The benzene solution was washed with dilute sodium carbonate and water, dried, and evaporated to give an oil. Extraction of the oil with benzene and evaporation gave 3-thiophenacylidene-5-phenyl-I,2-dithiole, (M.P. = I6I°C.) identical (mixed M.P. and infra-red spectrum) with an authentic specimen [44] prepared from dibenzoylacetone and phosphorus pentasulphide.

Yield = 0·I7g. = 56%.

REACTIONS OF DITHIOLIUM SALTS CAPABLE OF FORMING ANHYDROBASES BY LOSS OF A PROTON FROM A SIDE CHAIN.

3-Benzylidene-5-phenyl-I,2-dithiole.

3-Benzyl-5-phenyl-I,2-dithiolium perchlorate (0·5g.) was shaken with excess of dilute sodium carbonate or ammonia solution. The orange precipitate was collected and recrystallised from toluene. (M.P. = 173 - 175°C.)

Yield was quantitative.

$C_{16}H_{12}S_2$ requires C = 71·7%, H = 4·48%, S = 23·9%.

Found C = 71·8%, H = 4·4%, S = 23·5%.

Attempted synthesis of "thiothiophthens" or precursors by acylation of 3-methyl-5-phenyl-I,2-dithiolium salts.

Reaction of 3-methyl-5-phenyl-I,2-dithiolium perchlorate with benzoyl chloride.

Equimolar quantities of the reactants were heated under reflux in nitromethane for one hour. On cooling the solution deposited the unreacted dithiolium salt.

Reaction with methyl benzoate.

The salt was warmed with a slight excess of the ester until boiling. The mixture turned brown, and only unreacted dithiolium salt could be isolated from it.

5-Phenyl-3-thiophenacylidene-I,2-dithiole from 3-methyl-5-phenyl-I,2-dithiolium perchlorate.

The perchlorate (0·4g.) was boiled with methyldithiobenzoate (2 ml)[92] in a test tube for 5 minutes. The mixture was chromatographed on alumina in light petroleum (B.P.=40-60°) containing 10% benzene. Unreacted dithioester was eluted first. Two other bands were obtained which could not be completely resolved. From these was obtained a purple oil which was crystallised from toluene : light petroleum to furnish deep crimson plates. (M.P.=159 5-161°C). This product was identical (infra-red and mixed M.P.) to an authentic sample of the "thiothiophthen" prepared[44] by treatment of dibenzoylacetone with phosphorus pentasulphide.

Self-condensation of 3-methyl-5-phenyl-I,2-dithiolium perchlorate.

Pyridine (0·4 ml) was added to 3-methyl-5-phenyl-I,2-dithiolium perchlorate (1g.) dissolved in acetic acid (5 ml) and the solution was boiled briefly and left to cool. The product which crystallised was filtered off, and washed once each with ether, water and warm ethanol. It was recrystallised from nitromethane. (M.P.=218°C)

Yield = 0·42g. = 76%.

$C_{20}H_{16}S_2$ requires C = 75·0%, H = 5·0%, S = 20·0%.

Found C = 74·14%, H = 5·07%, S = 20·55%.

4,6-Diphenyl-2-thiophenacylidenethiopyran.

3,5-Diphenyl-I,2-dithiolium perchlorate (0·345g.) dissolved in a mixture of acetic acid (2 ml) and pyridine (0·5 ml), was added quickly to a hot solution of 3-methyl-5-phenyl-I,2-dithiolium perchlorate (0·292g.)in acetic acid (3 ml). The mixture was boiled briefly, and when it was cool, the precipitate which had formed was collected, and was washed once each with ethanol and hot water. The very deep purple product was crystallised from nitromethane. (M.P. = I94-6°C.)

Yield = 0·22g. = 58%.

$C_{25}H_{18}S_2$ requires C = 78·6%, H = 4·72%, S = I6·75%.

Found C = 78·22%, H = 5·05%, S = I6·8%.

The compound was identical (mixed M.P. and infrared spectrum) with a sample of 4,6-diphenyl-2-thiophenacylidenethiopyran prepared as described below.

4,6-Diphenyl-2-methylthiothiopyrylium perchlorate.

4,6-Diphenyl-2-thione (0·3g.) was dissolved in nitromethane (2 ml.) and methyl iodide (3 ml) was added. The mixture was left one day and filtered to produce 4,6-diphenyl-2-methylthiothiopyrylium iodide. (M.P. = I76°C. from acetic acid). This was converted to the perchlorate in acetic acid containing perchloric acid. (Darkens 240°C, M.P. = 247°C.)

Yield = 0·25g. = 59%.

$C_{18}H_{15}S_2ClO_4$ requires C = 55·4%, H = 4·3I%, S = I6·2%, Cl = 9·0%.

Found C = 54·78%, H = 3·99%, S = I5·I%, Cl = 9·I%.

4,6-Diphenyl-2-phenacylidenethiopyran.

To a suspension of sodium benzoyl acetate in ethanol, (prepared from benzoylacetic acid (0·32g.) and sodium ethoxide (0·046g. Na) in ethanol (25 ml.) was added 4,6-diphenyl-2-methylthiothiopyrylium iodide (0·42g.). The mixture was boiled briefly and filtered. Evaporation gave a red powder which was crystallised from ethanol. (M.P. = I39-I4I°C).

Yield = 0·2Ig. = 57%.

$C_{25}H_{18}SO$ requires C = 82·0%, H = 5·74%, S = 8·74%.

FOUND /

Found C = 81·5%, H = 4·77%, S = 9·54%.
C = 82·98%, H = 4·85%, S = 8·21%.

Sulphurisation of 4,6-diphenyl-2-phenacylidenethiopyran.

4,6-Diphenyl-2-phenacylidenethiopyran (100 mg) and phosphorus pentasulphide (500 mg) in benzene (10 ml) were heated under reflux for one hour. The solution was washed with water, filtered, and chromatographed on alumina in benzene. The purple band was collected and yielded 4,6-diphenylthiophenacylidenethiopyran.

Yield = 30 mg. = 29%.

Preparations of monomethine cyanine dyes.

Half milli-mole quantities of the methylthio and methyl dithiolium salts were boiled together in 3 mls of acetic acid and one drop of pyridine added. The cyanine dyes which crystallised on cooling were washed with water to remove pyridinium perchlorate and were recrystallised from acetic acid or acetic acid / dimethylformamide (4 / 1).

a). 2-Methylthio-4-phenyl-1,3-dithiolium perchlorate with 2-methyl-4-phenyl-1,3-dithiolium perchlorate.

The product was deep red plates with a yellow reflex.

Yield = 155 mg. = 67%. (M.P. = 234°C).

$C_{19}H_{13}S_4ClO_4$ requires C = 48·8%, H = 2·77%, S = 27·3%, Cl = 7·58%.
Found C = 48·76%, H = 2·78%, S = 27·4%, Cl = 7·62%.

b). 2-Methylthio-4-phenyl-1,3-dithiolium perchlorate with 3-methyl-5-phenyl-1,2-dithiolium perchlorate.

The product was deep violet needles with a yellow reflex. (M.P. = 250°C).

Yield = 100 mg. = 21%.

$C_{19}H_{13}S_4ClO_4$ requires C = 48·8%, H = 2·77%, S = 27·3%, Cl = 7·58%.
Found C = 48·3%, H = 2·80%, S = 27·62%, Cl = 7·62%.

3-Methylthio-5-phenyl-I,2-dithiolium perchlorate with 2-methyl-4-phenyl-I,3-dithiolium perchlorate.

Yield = 90 mg = I8%.

This had a poor analysis and its melting point was low (232°C). It should be the same as the cyanine prepared above. (M.P. = 250°C). A comparison of the infra-red spectra confirmed its identity.

c). 3-Methylthio-5-phenyl-I,2-dithiolium iodide with 3-methyl-5-phenyl-I,2-dithiolium perchlorate.

The product was violet needles with a green reflex.

Yield = 95 mg. = 2I%.

$C_{19}H_{13}S_4ClO_4$ requires C = 48·8%, H = 2·77%, S = 27·3%, Cl = 7·6%.

Found C = 48·03%, H = 3·40%, S = 27·0%, Cl = 8·05%.

d). 2-Benzoyl-4-phenyl-I,3-dithiolium perchlorate with 2-methylthio-4-phenyl-I,3-dithiolium perchlorate.

The product was deep violet needles with a yellow reflex.

M.P. = 292°C. (By Kofler block).

Yield = I50 mg. = 56%.

$C_{25}H_{17}S_4ClO_4$ requires C = 55·I%, H = 3·I3%, S = 23·55%, Cl = 6·52%.

Found C = 54·I3%, H = 3·32%, S = 2I·90%, Cl = 6·I0%.

e). 2-Methylthio-5-phenyl-I,2-dithiolium iodide with 2-benzyl-4-phenyl-I,3-dithiolium perchlorate. (crystallised from acetic acid perchloric acid).

The product was deep violet needles with a yellow reflux.

Yield = I40 mg. = 5I 5%. M.P. = 224-227°C.

$C_{25}H_{17}S_4ClO_4$ requires C = 55·I%, H = 3·I3%, S = 23·55%, Cl = 6·5%.

Found C = 52·4%, H = 3·04%, S = 23·65%, Cl = 9·03%.

Cl = 9·36%.

f). 3-Benzyl-5-phenyl-I,2-dithiolium perchlorate with 3-methylthio-5-phenyl-I,2-dithiolium iodide.

The compound obtained could not be obtained in a stable crystalline form. Above 100° it slowly melted to a purple oil.

Reactions of (I) 2-methyl-4-phenyl-1,3-dithiolium perchlorate and (II) 3-methyl-5-phenyl-1,2-dithiolium perchlorate with ethyl orthoformate.

The perchlorates (200 mg) were boiled with 100 mg of ethyl orthoformate in acetic acid for five minutes. The green oils obtained on cooling were triturated with ether, and crystallised from nitromethane. They were recrystallised from nitromethane : acetic acid (2 :1).

(I). Yield = 152 mg. = 48%. M.P. = 240°C.

$C_{21}H_{15}S_4ClO_4$ requires C = 51·2%, H = 3·04%, S = 25·3%, Cl = 7·2%.

Found C = 50·12%, H = 3·18%, S = 21·4%, Cl = 6·9%.

C = 49·98%, H = 3·54%, S = 23·2%, Cl = 8·3%.

(II). Yield = 42 mg. = 13%.

Softens at 160°C, gradually melt and decompose at 280°C.

Found C = 46·21%, H = 3·02%, S = 23·0%, Cl = 11·1%.

The analyses suggest contamination with starting material, especially in the case of the second compound.

The following are the $\log_{10}\varepsilon$ values against the corresponding λ max. values of the compounds given. Values in parentheses refer to shoulders on the curves, and (i) refers to inflexions on the curves. The spectral data refers to compounds in ethanolic solution in I cm. silica cells.

COMPOUND.	λ max in mμ.	$\log_{10}\varepsilon$
4-Phenylisothiazole.	(271) i 269 (267) i 241·5 210	(3·998) 4·026 (4·000) 4·031 4·206
Bis-(4-Phenyl-1,2-dithiole-3-yl) sulphide.	306 232	4·335 4·380
1,3-Dithiolium perchlorate.	253·5 211	3·582 3·533
4-Phenyl-1,3-dithiolium perchlorate.	305 229·5	3·888 4·018
Cis-Phenylmalondialdehydedianil.	403·5 287 247 211	4·296 4·233 4·097 4·130
Trans-Phenylmalondialdehydedianil.	(370) 310·5 250 (225)	(3·8) 4·428 3·863 (4·005)

I-Anilino-3-phenylprop-I-ene-3-thione.	440 324 250 236 225	4·387 4·072 4·033 4·040 4·026
I-Methylanilino-3-phenylprop-I-ene-3-thione.	440 319 255 211	4·236 4·066 4·043 4·235
I-Anilino-3,5-diphenylprop-I-ene-3-thione.	435 313 232	4·340 4·095 4·127
4,6-Diphenylthiopyran-2-one.	369 (290) 265 (221) 212	3·915 (4·043) 4·360 (4·290) 4·38
4,6-Diphenylthiopyran-2-thione.	480 309 242	3·851 4·436 4·268
3-(p-methylamino)-phenyl-5-phenyl-I,2-dithiolium perchlorate.	555 356 (340) (255) 211	4·605 4·142 4·128 3·840 4·125
7-Dimethylamino-2,4-diphenylbenzothiopyrylium perchlorate.	565 333 262 230 220	4·430 4·650 4·640 4·491 4·495

3-Phenacylidene-5-phenyl-I,2-dithiole.	455 (300) i (265) 235 212	4·390 4·149 (4·227) 4·430 4·412
5-Phenyl-3-thiophenacylidene-I,2-dithiole.	512 305 252 225 206	4·199 4·403 4·773 4·552 4·626
4,6-Diphenyl-2-phenacylidene-thiopyran.	475 (376) 365 290 (282) 250	4·130 (3·970) 3·982 4·242 (4·204) 4·224
4,6-Diphenyl-2-thiophenacylidene-thiopyran.	535 428 (320) i (290) i 260	4·075 3·552 3·950 4·075 4·214
4-Methyl-6-phenyl-2-thiophenacylidene-thiopyran.	518 388 345 258 225	3·985 3·310 3·646 4·136 4·164
Cyanine (CIXIIIa).	523 335 253 209	4·732 3·483 4·212 4·332

Cyanine (CLXIIIb).	528 348 253 210	2·745 3·304 4·264 4·550
Cyanine (CLXIIIc).	554 347 246 223	4·681 3·970 4·260 4·280
Cyanine (CLXIIId).	555 354 246 210	4·680 4·206 4·265 4·453
Cyanine (CLXIIIe).	568 368 350 267 (258) 249	4·598 3·942 4·010 4·421 (4·22) 3·823
2,4,5-Triphenyl-1,3-dithiole.	342 228	3·545 4.304
2-Amino-2,4,5-triphenyl-1,3-dithiole.	344 317 230 212	3·740 3·723 4·440 4·625
2-Ethoxy-2,4,5-triphenyl-1,3-dithiole.	335 295 270 227	3·700 3·832 3·840 4·461

2-Cyano-2,4,5-triphenyl-I,3-dithiole.	355 (233) i 208·5	3·618 (4·49) i 4·645.

Fig 1

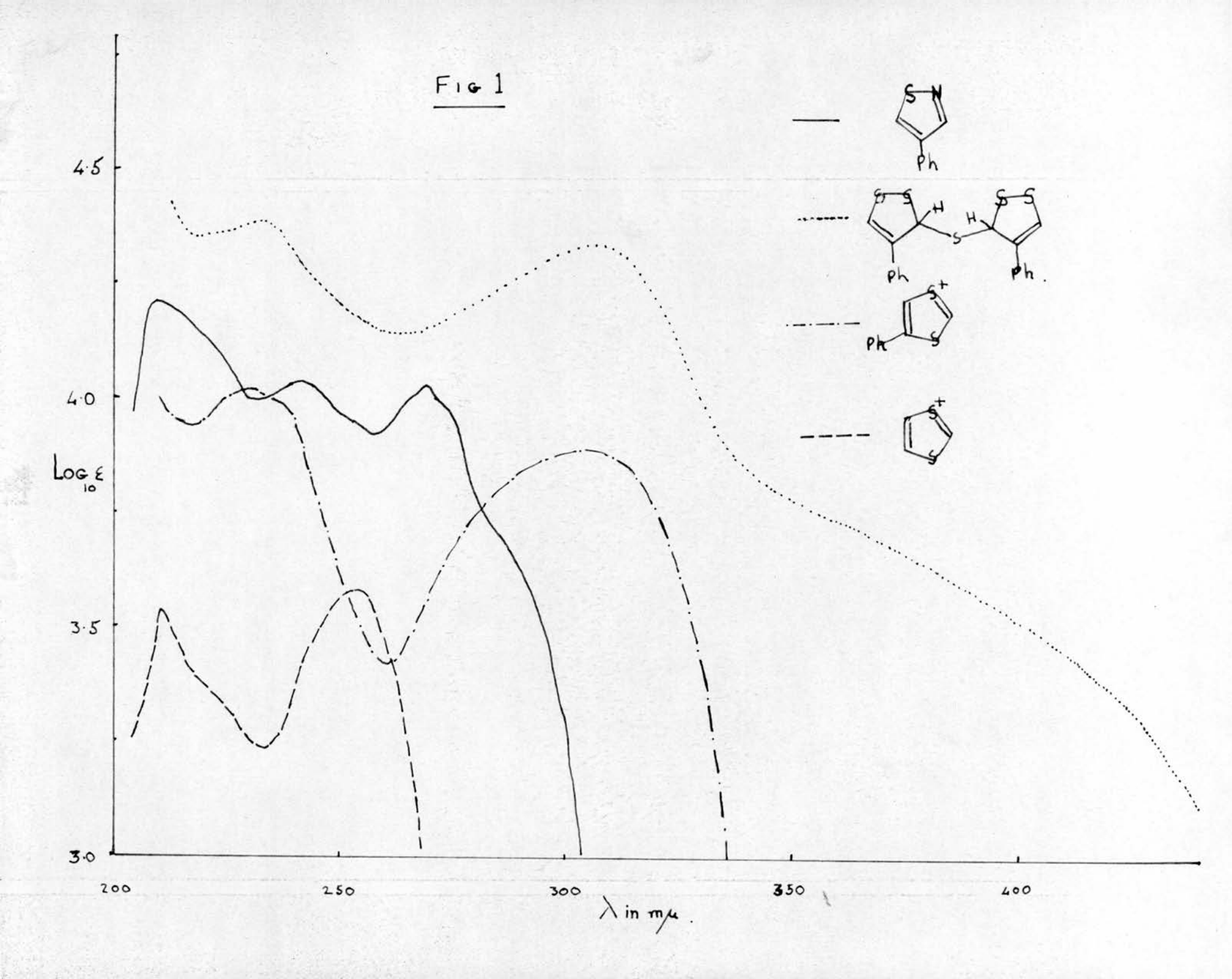
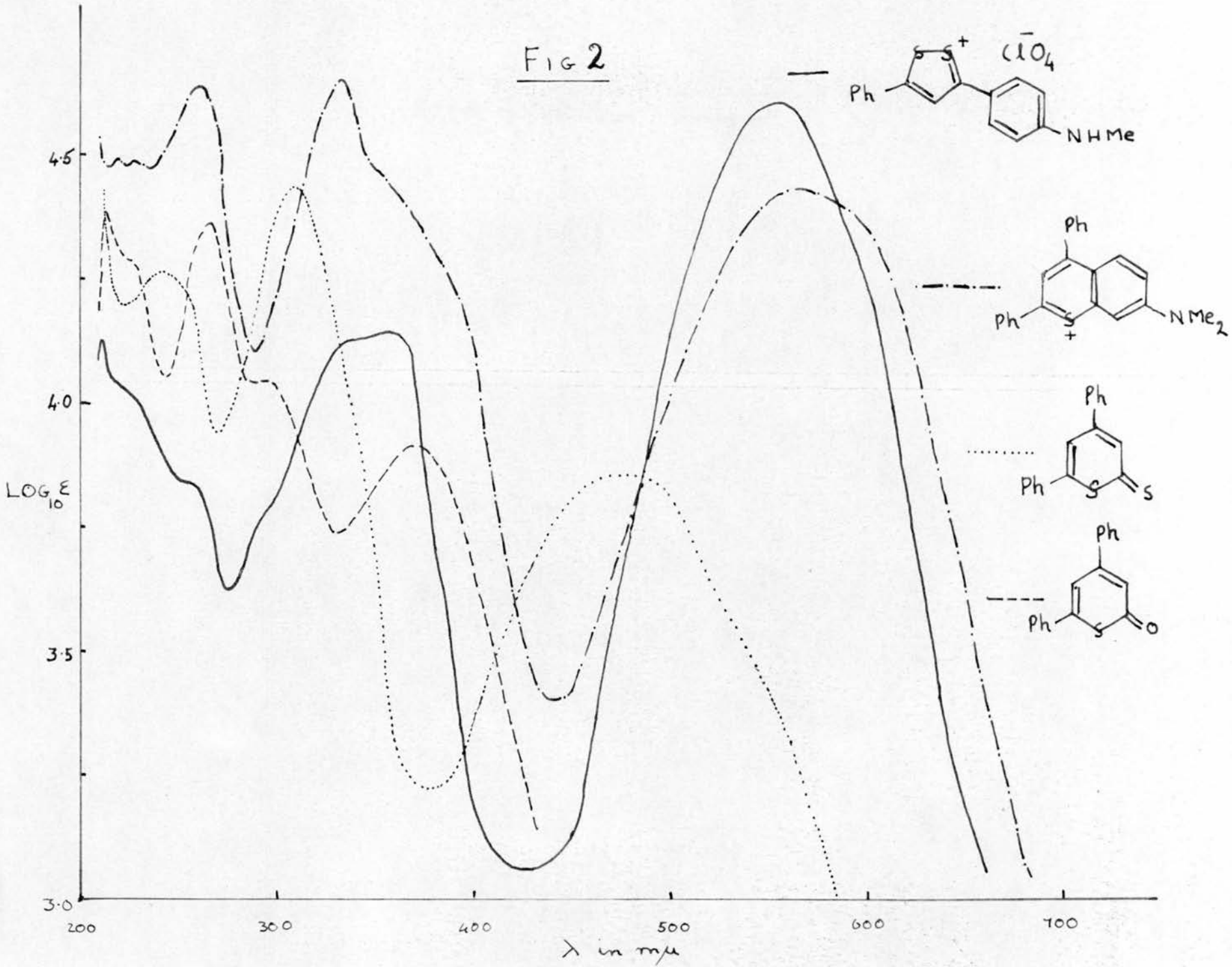


FIG 2


4·5
4·0
3·5
3·0
LOG ε
10
200
300
400
500
600
700
λ in mμ
Ph
NHMe
ClO4
NMe2
S
O

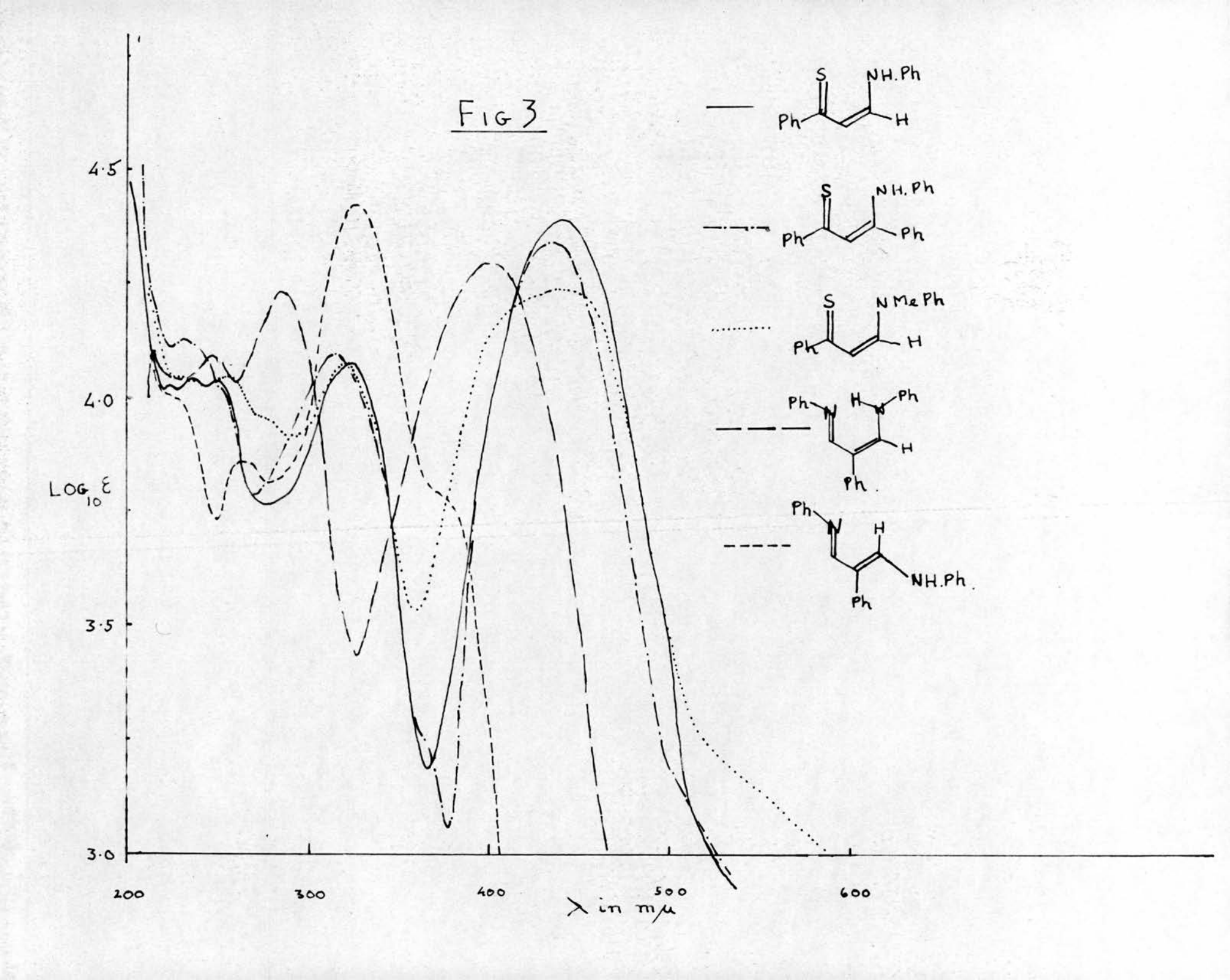


FIG 3
4·5
4·0
3·5
3·0
LOG10 ε
200
300
400
500
600
λ in mμ
S
NH.Ph
Ph
H
S
NH.Ph
Ph
Ph
S
NMePh
Ph
H
Ph
N
H
N
Ph
H
Ph
Ph
N
H
NH.Ph
Ph

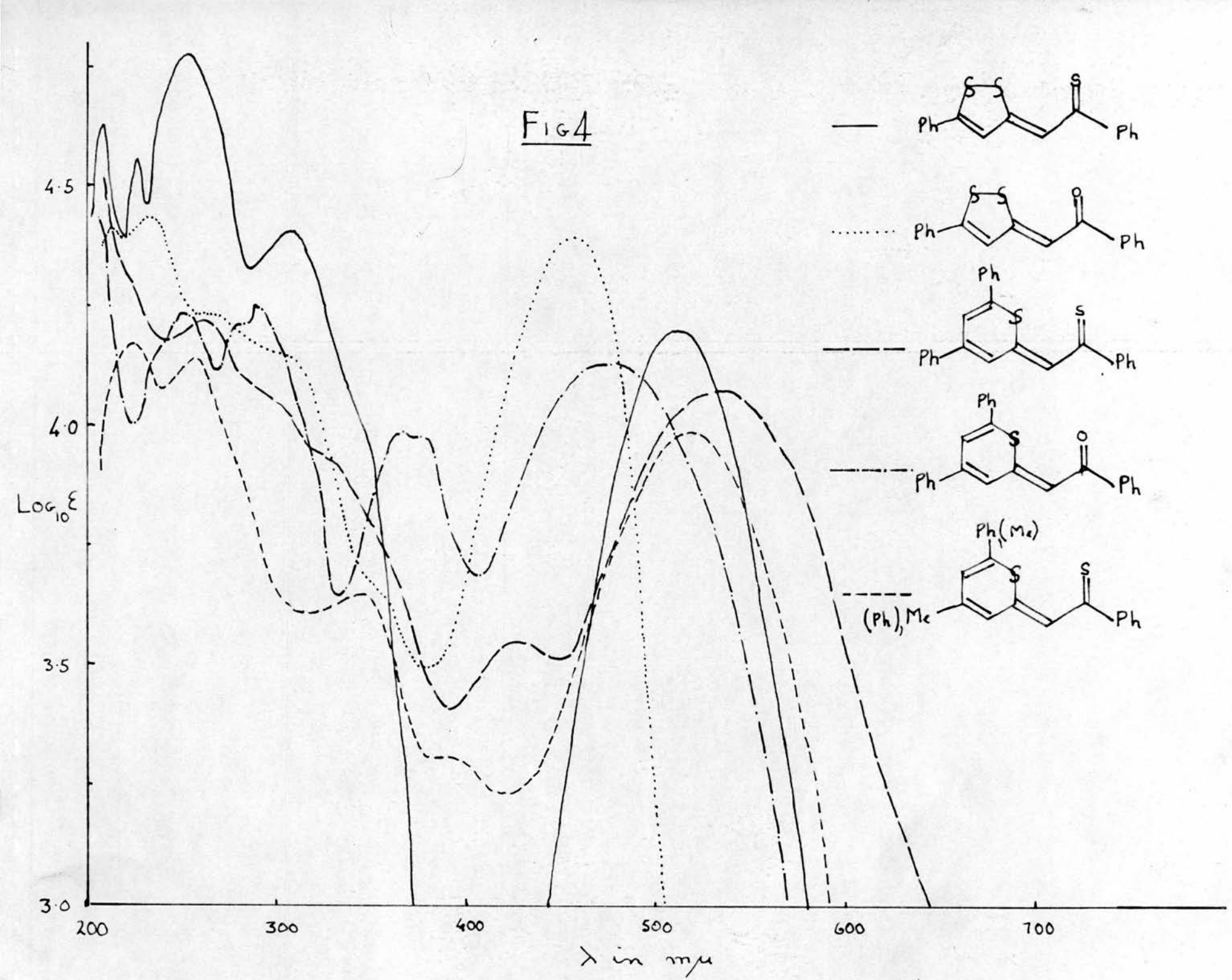
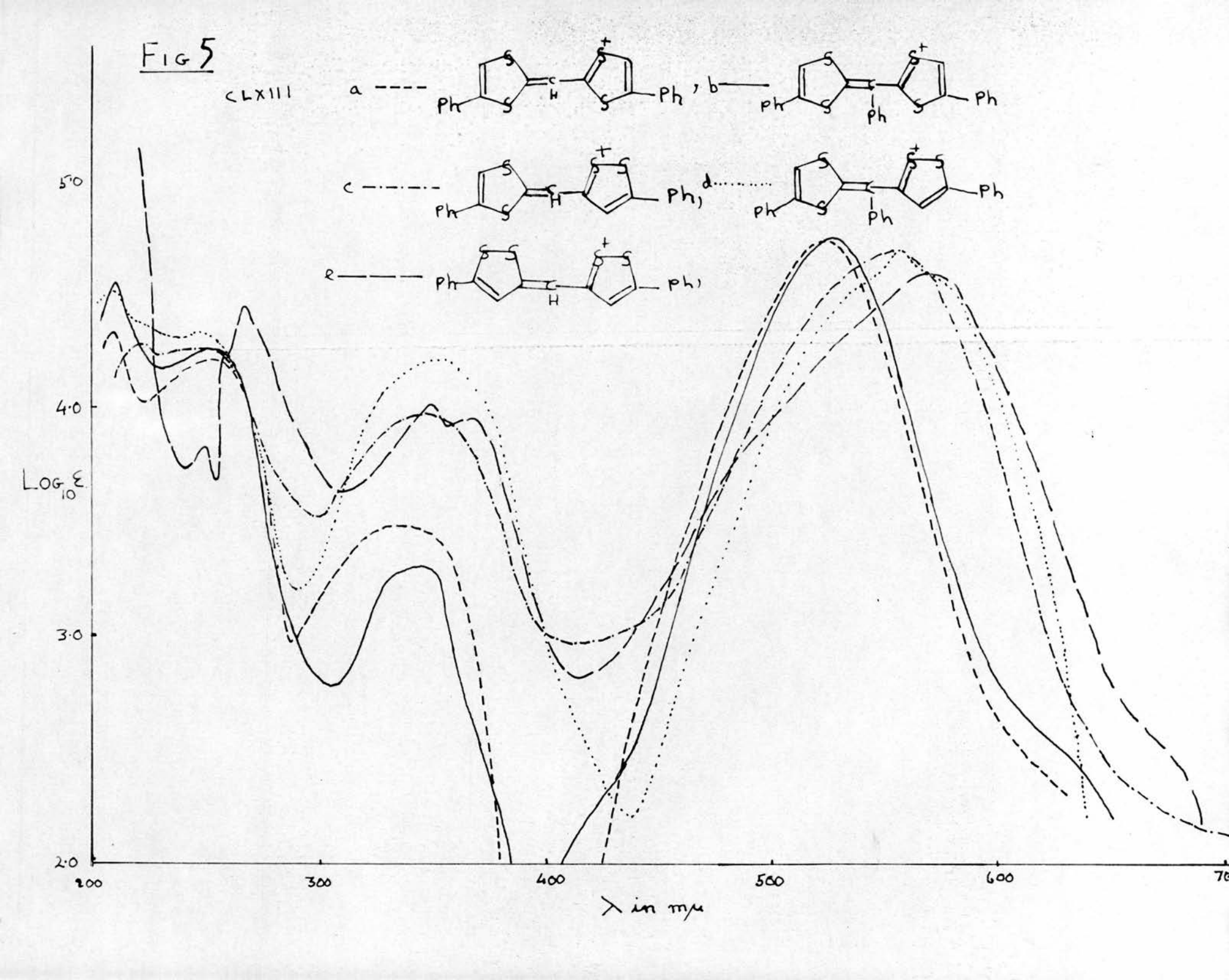


FIG 4
4·5
4·0
3·5
3·0
Log10 ε
200
300
400
500
600
700
λ in mμ
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph(Me)
(Ph), Me
Ph

FIG 5

CLXIII



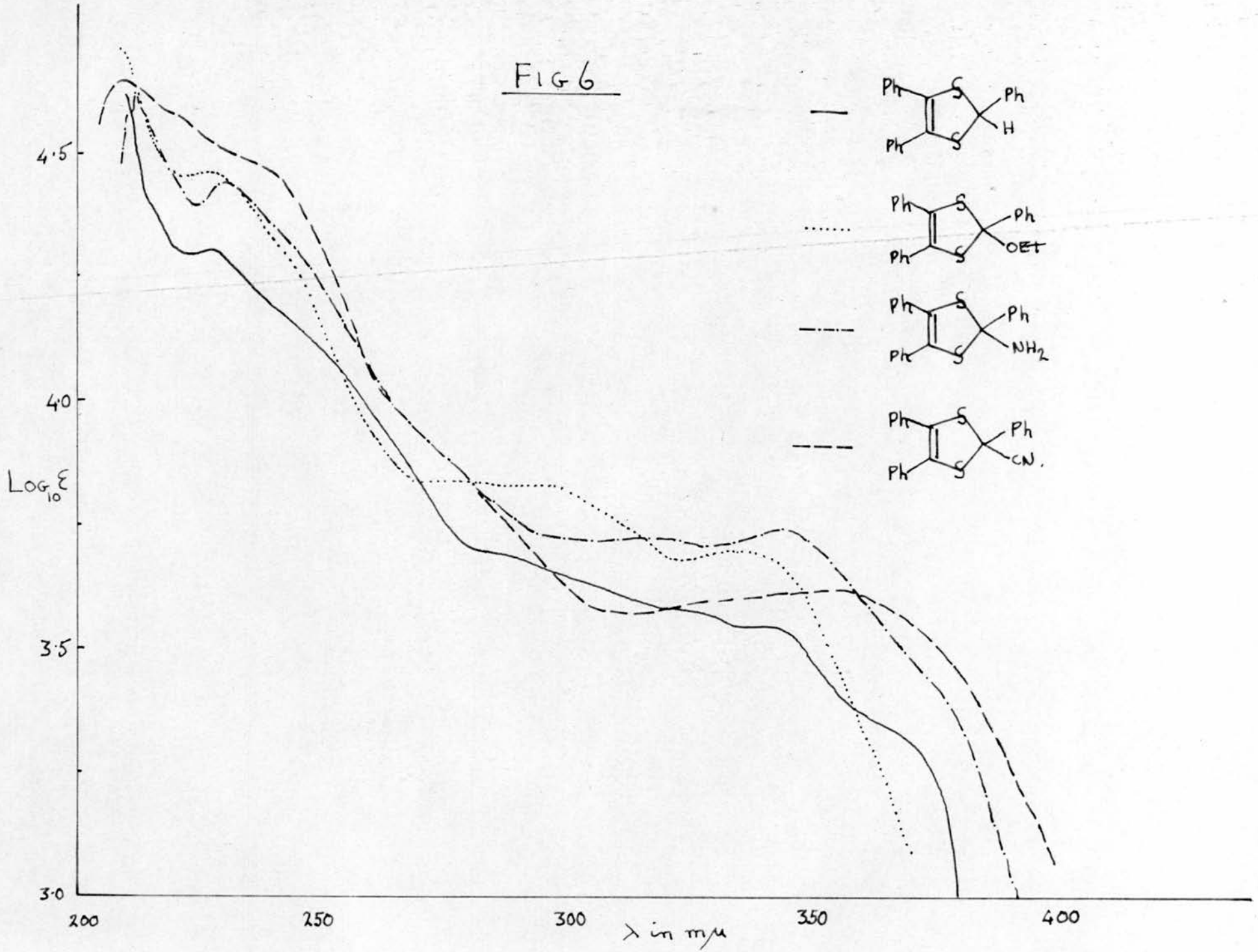


FIG 6
Ph
S
Ph
H
OEt
NH2
CN.
4·5
4·0
3·5
3·0
Log10 ε
200
250
300
350
400
λ in mμ

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Ultraviolet and Visible Absorption Spectra.—The absorption maxima of dithiolium salts, measured (unless otherwise stated) for ethanol solutions containing a little perchloric acid, with a Unicam S.P. 500 quartz spectrophotometer, are recorded in Table 2.

3,4-*Diphenylthiophen Derivative.*—Sodium phenyl(dithioacetate) (2·5 g.) in water (12·5 ml.) was added slowly to phenacyl bromide (2·2 g.) in boiling ethanol (50 ml.), and the solution was boiled for a further 10 min. Dilution with water, extraction with ether, and evaporation of the alkali-washed and dried ($CaCl_2$) extract gave a red oil. This was chromatographed in benzene on alumina; the eluted orange oil crystallised from light petroleum (b. p. 40—60°) by cooling to −70°, affording a pale yellow solid (putative 3,4-*diphenylthiophen-2-thiol* or a tautomer) (2·03 g.), m. p. 60—62° (Found: C, 72·2; H, 4·2; S, 23·45. $C_{16}H_{12}S_2$ requires C, 71·6; H, 4·5; S, 23·8%). The compound (0·2 g.) was treated with Raney nickel (large excess) in boiling ethanol for 1 hr., the nickel was removed, and the solution was diluted with water. After 2 days at room temperature crystals of *meso*-2,3-diphenylbutane, m. p. 125° (lit.,[15] m. p. 126—127°), had separated.

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chloride and were decomposed by shaking them with saturated aqueous sodium sulphide. The thiones were recovered by extraction of the resulting mixed solids with hot ethanol or acetone (and, in the case of the unsubstituted compound, by extraction of the sodium sulphide solution with ether).

Methyl phenacyl trithiocarbonate and *O*-ethyl *S*-phenacyl dithiocarbonate gave 4-phenyl-1,3-dithiole-2-thione (35%), reddish-brown needles, m. p. 117—118° (from ethanol) (lit.,[12] m. p. 116°) (Found: C, 51·4; H, 2·4; S, 45·85. Calc. for $C_9H_6S_3$: C, 51·4; H, 2·9; S, 45·7%).

O-Ethyl *S*-acetonyl dithiocarbonate gave 4-*methyl*-1,3-*dithiole*-2-*thione* (23%), yellow plates, m. p. 30° after chromatography (in benzene) on alumina and recrystallisation from light petroleum (b. p. 40—60°) (Found: C, 32·8; H, 3·0; S, 64·2. $C_4H_4S_3$ requires C, 32·4; H, 2·7; S, 64·9%).

O-Ethyl *S*-2′-oxoethyl dithiocarbonate gave 1,3-dithiole-2-thione (8%), m. p. and mixed m. p. 49—50° (lit.,[13] m. p. 50°) after chromatography (in benzene) on alumina and recrystallisation from light petroleum (b. p. 40—60°).

Dithiolium Salts by Oxidation of Dithiolethiones.—(*a*) 1,2-*Dithiolium perchlorate*. 1,2-Dithiole-3-thione [14] (0·4 g.) in acetic acid (10 ml.) was treated with 30% hydrogen peroxide (1 ml.), the temperature being kept below 40°. After 20 min. the solution was filtered, treated with 70% perchloric acid (0·5 ml.) and diluted with ether, to precipitate 1,2-*dithiolium perchlorate* (0·3 g.), no definite m. p., which recrystallised from acetic acid containing a little perchloric acid (Found: C, 17·7; H, 1·5; Cl, 18·1; S, 32·4. $C_3H_3ClO_4S_2$ requires C, 17·8; H, 1·5; Cl, 17·5; S, 31·6%).

(*b*) 1,3-*Dithiolium perchlorate*. 1,3-Dithiole-2-thione (0·47 g.) in acetic acid (8 ml.) was treated with 30% hydrogen peroxide (1·2 ml.) with stirring and cooling to below 30°, and after 1 hr. the solution was decanted from an oil which had been formed. Dilution with ether caused separation of a mixture of oil and water which, on treatment in methanol (5 ml.) with 70% perchloric acid (3 drops) and ether (5 ml.), afforded 1,3-*dithiolium perchlorate* (0·14 g.), m. p. 264° (from acetic acid–perchloric acid) (Found: C, 18·3; H, 1·5; Cl, 17·15; S, 31·6%).

(*c*) 4-*Phenyl*-1,3-*dithiolium salts*. 4-Phenyl-1,3-dithiole-2-thione (0·21 g.) in acetone (5 ml.) and acetic acid (5 ml.) was treated with 30% hydrogen peroxide (0·34 ml.), and the solution was stirred for 10 min. and set aside for 1 hr. The solution was decanted into ether (20 ml.), and the resulting precipitate was treated with charcoal in, and recrystallised from, acetic acid containing a little sulphuric acid, to give 4-*phenyl*-1,3-*dithiolium hydrogen sulphate* (0·1 g.), m. p. 180° (became brown, solidified, and remelted at 232°) (Found: C, 39·2; H, 3·1; S, 35·15. $C_9H_8O_4S_3$ requires C, 39·1; H, 2·9; S, 34·8%). Treatment, in acetic acid, with perchloric acid yielded the *perchlorate*, m. p. 161° (Found: C, 38·8; H, 2·7; Cl, 12·55; S, 23·15. $C_9H_7ClO_4S_2$ requires C, 38·7; H, 2·5; Cl, 12·7; S, 23·0%).

Condensation of Dithiolium Salts with p-*Dimethylaminobenzaldehyde*.—2-Methyl-4-phenyl-1,3-dithiolium perchlorate (0·1 g.) and *p*-dimethylaminobenzaldehyde in acetic acid (3 ml.) were boiled for 5 min. and cooled to yield 2-p-*dimethylaminostyryl*-4-*phenyl*-1,3-*dithiolium perchlorate* (0·085 g.), deep blue needles, m. p. 203—204° (Found: C, 53·3; H, 3·9; Cl, 8·65; N, 3·2; S, 15·45. $C_{19}H_{18}ClNO_4S_2$ requires C, 53·8; H, 4·25; Cl, 8·5; N, 3·3; S, 15·1%).

3-Methyl-5-phenyl-1,2-dithiolium perchlorate (0·1 g.) similarly yielded 3-p-*dimethylaminostyryl*-5-*phenyl*-1,2-*dithiolium perchlorate* (0·1 g.), green needles, m. p. 214—215° (Found: C, 53·7; H, 4·1; Cl, 8·05; N, 3·5; S, 14·9%).

TABLE 2.

Absorption spectra of dithiolium perchlorates.

Compound	$\lambda_{max.}$ (mμ) with log ε (in parentheses)			
Ia		233 (4·01)		381 (4·36)
Ib	219 (3·98)		295 (3·84)	354 (4·33)
IIa	218 (4·16)	242 (4·20)	305 (3·80)	392 (4·20)
II; Ph_3	221 (4·40)		303 (3·98)	399 (4·18)
IIc	209 (4·05)		269 (3·57)	362 (4·19)
IIb		232 (4·06)	310 (3·89)	
IIf		232 (4·01)	306 (3·88)	
Ie		245 (3·62)	288 (3·59)	
IIe	212 (3·53)	254 (3·58)		
Ig *		263 (3·97)	363 (4·17)	644 (4·49)
IIg *		250 (4·20)	332 (3·89)	636 (4·72)

* In 10% aqueous ethanol.

perchloric acid gave 2,4-*diphenyl*-1,3-*dithiolium perchlorate*, yellow plates, m. p. 209—210° (Found: C, 50·0; H, 3·0; Cl, 10·2; S, 18·4%).

After 4 days at room temperature, phenacyl dithioacetate (0·5 g.) in ether (25 ml.) containing boron trifluoride (2 ml.; BF_3,Et_2O), yielded a salt which was converted into 2-*methyl*-4-*phenyl*-1,3-*dithiolium perchlorate* (0·23 g., 37%), plates, m. p. 160—161° (from acetic acid containing a little perchloric acid) (Found: C, 40·75; H, 2·9; Cl, 12·05; S, 21·9%).

(*b*) *Method A.* Solutions of the esters in ether (20 ml. per g. of ester) were saturated with hydrogen chloride and hydrogen sulphide and left at room temperature. The salts which crystallised were, in most instances, converted in acetic acid into the perchlorates.

Phenacyl dithiobenzoate gave (after 4 days) 2,4-diphenyl-1,3-dithiolium perchlorate (98%), m. p. 209—210°.

S-Phenacyl thiobenzoate [9] gave (after 6 weeks) a salt (*ca.* 95%), m. p. 144—145°, intermediate in composition between 2,4-diphenyl-1,3-dithiolium chloride and the dithiolium hydrogen dichloride (Found: C, 56·7; H, 3·75; Cl, 17·4; S, 20·2. Calc. for $C_{15}H_{11}ClS_2$: C, 62·0; H, 3·8; Cl, 12·2; S, 22·0. Calc. for $C_{15}H_{12}Cl_2S_2$: C, 55·0; H, 3·7; Cl, 21·7; S, 19·6%).

Acetonyl dithiobenzoate gave (after 3 days) 4-*methyl*-2-*phenyl*-1,3-*dithiolium perchlorate* (46%), pale yellow plates, m. p. 102—103° (from acetic acid) (Found: C, 41·35; H, 3·2; Cl, 12·2; S, 21·8%).

Phenacyl dithioacetate gave (after 3 weeks) 2-methyl-4-phenyl-1,3-dithiolium perchlorate (79%), m. p. 160—161°; use of boron trifluoride instead of hydrogen chloride gave 85% after 4 days.

Phenacyl phenyl(dithioacetate) (with boron trifluoride instead of hydrogen chloride) gave (after 24 hr.) 2-benzyl-4-phenyl-1,3-dithiolium perchlorate (74%), m. p. 113° (lit.,[5] m. p. 113°), which with aqueous sodium carbonate afforded 2-benzylidene-4-phenyl-1,3-dithiole, m. p. 204° (lit.,[5] m. p. 205—207°), $\lambda_{max.}$ 354 mμ (log ε 4·34) in dioxan [lit.,[5] 354 (4·33) in tetrahydrofuran].

(*c*) *Method B.* Hydrogen sulphide was passed for 1·5—3 hr. through boiling solutions of the esters in acetic acid (15 ml. per g. of ester) containing 70% perchloric acid (1 ml. per g. of ester). The dithiolium perchlorates crystallised from the cooled solutions and further crops were obtained by addition of ether to the mother-liquors.

α-Phenylphenacyl dithiobenzoate gave 2,4,5-*triphenyl*-1,3-*dithiolium perchlorate* (60%), yellow needles, m. p. 254—255° (from acetic acid) (Found: C, 58·2; H, 3·5; Cl, 8·5; S, 14·8. $C_{21}H_{15}ClO_4S_2$ requires C, 58·5; H, 3·5; Cl, 8·2; S, 14·9%).

S-Phenacyl thiobenzoate gave 2,4-diphenyl-1,3-dithiolium perchlorate (43%), m. p. 209—210°.

S-Phenacyl thioacetate gave 2-methyl-4-phenyl-1,3-dithiolium perchlorate (33%), m. p. 160—161°.

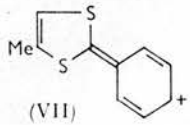
S-α-Phenylphenacyl thiobenzoate [10] (2 g.) gave tetraphenylthiophen (1 g.), m. p. 184—185° (lit.,[11] m. p. 184°), shown by its infrared spectrum to be identical with an authentic specimen. Dilution of the mother-liquors with ether yielded 2,4,5-triphenyl-1,3-dithiolium perchlorate (0·3 g.). Under the same conditions, but without hydrogen sulphide, the thioester gave tetraphenylthiophen in the same yield.

Methyl Phenacyl Trithiocarbonate.—Methanethiol (12 ml.) and, afterwards, carbon disulphide (17·4 g.) were added, below 0°, to ethanol (200 ml.) containing sodium ethoxide (from 5·3 g. of sodium). Phenacyl bromide (45 g.) in ethanol (200 ml.) was then added and the solution was left at room temperature for 1 hr. and poured into water (1·5 l.). The product which separated recrystallised from light petroleum (b. p. 60—80°), to yield *methyl phenacyl trithiocarbonate* (41·8 g.), yellow needles, m. p. 40—41° (Found: C, 49·3; H, 4·2; S, 39·7. $C_{10}H_{10}OS_3$ requires C, 49·6; H, 4·1; S, 39·9%). Attempted cyclisations by methods A and B failed.

O-*Ethyl* S-*Acetonyl and* O-*Ethyl* S-2′-*Oxoethyl Dithiocarbonate.*—Bromoacetone and chloroacetaldehyde were allowed to react with potassium *O*-ethyl dithiocarbonate in ethanol for 1 hr. at 0°. The solutions were then poured into water, and the oils which separated were dried ($CaCl_2$) in ether and used without purification.

1,3-*Dithiole*-2-*thiones.*—The di- and tri-thiocarbonates were heated with phosphorus pentasulphide (2—3 mol.) in boiling tetralin (10—20 ml. per g. of ester) for 20 min. The cooled solutions were decanted into twice their volume of ether, washed successively with water, 10% sodium hydroxide solution, and water, and dried ($CaCl_2$). The thione–mercuric chloride complexes were then precipitated by pouring the solutions into saturated methanolic mercuric

An unexpected reaction occurred when phenacyl bromide was allowed to react with sodium phenyl(dithioacetate) in boiling ethanol; analysis suggested that the product had been formed from the expected dithioester (IX) by loss of water, and was possibly, therefore, the thiophenthiol (X) or one of its thione tautomers. Evidence in support of such a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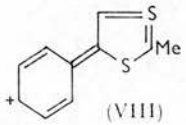
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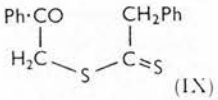
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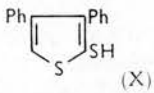

(X)

structure was provided by hydrogenolysis with Raney nickel to *meso*-2,3-diphenylbutane. Subsequent preparations of the ester (IX) were conducted below room temperature and with neutralisation of the excess of alkali in the sodium phenyl(dithioacetate) solution.

Experimental

1,2-*Dithiolium Salts from Hydrogen Disulphide.*—Hydrogen disulphide was prepared by the method of Fehér, Laue, and Winkhaus.[7] Dibenzoylmethane (3 g.), in dry benzene (100 ml.) saturated with hydrogen chloride, was treated with the disulphide (2 ml.) and left at room temperature for 3 days. The solution deposited a chloride (1·5 g.), pale yellow needles, m. p. 137°, which yielded unsatisfactory analytical results. Treatment of this, in acetic acid, with perchloric acid gave 3,5-*diphenyl*-1,2-*dithiolium perchlorate* (1·1 g.), pale yellow needles, m. p. 258—259° (Found: C, 50·9; H, 3·0; Cl, 9·4; S, 17·95. $C_{15}H_{11}ClO_4S_2$ requires C, 50·8; H, 3·1; Cl, 10·0; S, 18·0%).

Benzoylacetone (4 g.), treated similarly, yielded a chloride, m. p. 46—48°, which was converted into 3-*methyl*-5-*phenyl*-1,3-*dithiolium perchlorate* (7·2 g.), needles, m. p. 114—115° (from acetic acid–butyl acetate) (Found: C, 41·3; H, 3·2; Cl, 12·1; S, 21·95. $C_{10}H_9ClO_4S_2$ requires C, 41·0; H, 3·1; Cl, 12·1; S, 21·9%).

Thioesters and Dithioesters.—Dithioacids were prepared from Grignard reagents and carbon disulphide, and aqueous solutions of the sodium salts were purified as described by Bost and Shealy.[8] Addition of the halogeno-ketone (1 mol.; phenacyl bromide, α-phenylphenacyl chloride, or bromoacetone) in an equal volume of ethanol, and heating at 75—80° for a minute, gave the dithioesters which were isolated by filtration or extraction with ether. Thioesters were prepared similarly from the commercially available thioacids.

Conditions for the preparation of phenacyl phenyl(dithioacetate) were more critical: an aqueous 1·25M-solution (35 ml.; freed from alkali by titration with hydrochloric acid until dithioacid began to separate) of sodium phenyl(dithioacetate) was added slowly to phenacyl bromide (7·2 g.) in ethanol (200 ml.), and more ethanol was added to give a clear solution. The solution, after being left at 0° for 1 hr., diluted with water until cloudy, and set aside for 15 hr., deposited the dithioester (52%).

M. p.s and analyses of the esters are in Table 1. Acetonyl dithiobenzoate was a red oil that was not purified.

Table 1.

Thioesters and dithioesters.

			Found (%)				Required (%)		
Phenacyl ester	M. p.	Form	C	H	S	Formula	C	H	S
Thioacetate	42—43°	Colourless plates *	62·1	5·4	16·5	$C_{10}H_{10}O_2S$	61·9	5·2	16·5
Dithioacetate	48—49	Yellow needles †	56·4	4·5	30·6	$C_{10}H_{10}OS_2$	57·1	4·8	30·5
Dithiobenzoate	75—76	Red ,, ‡	65·7	4·3	23·6	$C_{15}H_{12}OS_2$	66·2	4·4	23·5
Phenyl(dithioacetate)	48	Yellow ,, †	67·1	4·9	22·3	$C_{16}H_{14}OS_2$	66·75	4·9	22·4
(α-Phenylphenacyl dithiobenzoate) ...	102—103	Red plates §	72·5	4·9	17·9	$C_{21}H_{16}OS_2$	72·4	4·6	18·4

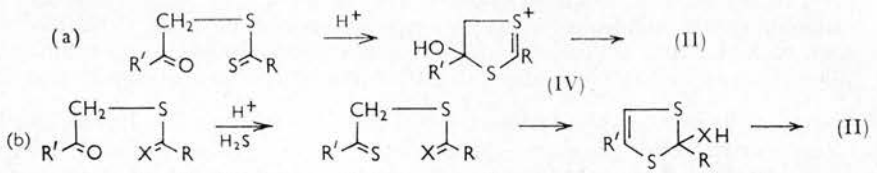
* From ether. † From light petroleum (b. p. 40—60°). ‡ From acetic acid. § From light petroleum (b. p. 80—100°).

1,3-*Dithiolium Salts by Cyclisation of Esters.*—(*a*) *Without hydrogen sulphide.* Ether (100 ml.) containing phenacyl dithiobenzoate (5 g.) was saturated with hydrogen chloride and left at room temperature for 3 weeks. The solution slowly deposited a chloride (2·1 g., 40%), yellow prisms, which yielded unsatisfactory analytical results. Treatment of this, in acetic acid, with

points and ultraviolet spectra to the known 2-benzyl-4-phenyl-1,3-dithiolium perchlorate (IId) and 2-benzylidene-4-phenyl-1,3-dithiole (III) which were obtained [5] as photolysis products of 4-phenyl-1,2,3-thiadiazole.

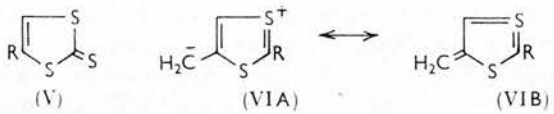
The function of hydrogen sulphide in these cyclisations is probably to convert the carbonyl group of the ester into a thiocarbonyl group, so allowing the reaction to take place according to scheme 2(b) (X = S) rather than 2(a) which involves a less probable intermediate (IV). If the necessary hydrogen sulphide is not added, it may be formed by decomposition of half of the starting material, so that yields of the salt cannot then exceed 50%. It follows from this hypothesis that dithiolium salts might also be formed according to Scheme 2(b) (X = O). When method A was used, *S*-phenacyl thiobenzoate

Scheme 2.



slowly gave the chloride (IIa), but *S*-phenacyl thioacetate failed to cyclise; both esters, however, readily gave the dithiolium perchlorates (IIa) and (IIb) by method B and this is the most convenient route to these particular salts. *S*-α-Phenylphenacyl thiobenzoate gave only a very low yield of a dithiolium salt by method B. The main product, tetraphenylthiophen, which was also produced in the absence of hydrogen sulphide, is thought to arise by hydrolysis to α-mercaptodeoxybenzoin, self-condensation of this to tetraphenyl-1,4-dithiin, and extrusion of a sulphur atom. The last reaction is known to occur readily.[5]

Methyl phenacyl trithiocarbonate and *O*-ethyl *S*-phenacyl dithiocarbonate failed to yield dithiolium salts but, with phosphorus pentasulphide in boiling tetralin, both esters yielded 4-phenyl-1,3-dithiole-2-thione (V; R = Ph). Similar reactions afforded 1,3-dithiole-2-thione (V; R = H) and its 4-methyl derivative (V; R = Me). Treatment of the thiones (V; R = H and Ph) in acetic acid with hydrogen peroxide (conditions similar to those described by Klingsberg [2] for the 1,2-dithiole-3-thiones) yielded 1,3-dithiolium perchlorate (IIe) and its 4-phenyl derivative (IIf). 5-Thio-1,2-dithiole-3-carboxylic acid was previously [2a] used as the source of the unsubstituted 1,2-dithiolium cation (Ie) but we found that the unsubstituted thione also yields this cation on treatment with peracetic acid.



The methyldithiolium perchlorates (Ib) and (IIb) with *p*-dimethylaminobenzaldehyde in boiling acetic acid rapidly gave the *p*-dimethylaminostyryl compounds, and they are, therefore, comparable in reactivity with 2-methylbenzo-1,3-dithiolium salts.[6] The perchlorate (IIc), however, failed to react in acetic acid or acetic anhydride, even in the presence of pyridine or triethylamine; evidently the conjugate bases of 4-methyl-1,3-dithiolium cations are not effectively stabilised by *d*-orbital resonance (VIA ⟷ VIB).

The ultraviolet absorption spectra of the dithiolium salts are given in Table 2. When the structure permits positive charge delocalisation over one or more phenyl groups [as, *e.g.*, in (VII)] there is strong absorption in the region 350—400 mμ, but 4-phenyl- and 2-methyl-4-phenyl-1,3-dithiolium perchlorate (IIf and IIb), in which interannular conjugation of this type is impossible without participation (VIII) of sulphur *d*-orbitals, absorb at lower wavelengths (305—310 mμ). Klingsberg [2b] observed similar differences between the spectra of 3- and 4-phenyl-1,2-dithiolium salts.

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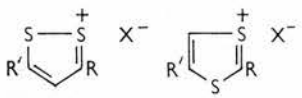
984. *The Dithiole Series. Part I.*[1] *Synthesis of* 1,2- *and* 1,3-*Dithiolium Salts.*

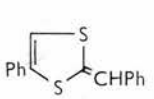
By D. Leaver, W. A. H. Robertson, and D. M. McKinnon.

Reaction of hydrogen disulphide with β-diketones in presence of a strong acid yields 1,2-dithiolium salts. *S*-α-Oxoalkyl thio- and dithio-carboxylates are cyclised by treatment with hydrogen sulphide and a strong acid, yielding 1,3-dithiolium salts. Suitably placed methyl groups in both types of dithiolium salt condense with *p*-dimethylaminobenzaldehyde. *O*-Ethyl *S*-α-oxoalkyl dithiocarbonates with phosphorus pentasulphide afford 1,3-dithiole-2-thiones which are oxidised to dithiolium salts by peracetic acid.

The chemistry of the heterocyclic cations (I) and (II) (dithiolium salts) has received little attention and, until recently, few general methods for the synthesis of such compounds were known. We have developed routes to diaryl- and alkylaryl-1,2- and -1,3-dithiolium salts, and Klingsberg [2] has reported a synthesis of 1,2-dithiolium salts (including the parent compound) by treatment of 1,2-dithiole-3-thiones with peracetic acid.



(I) (II)

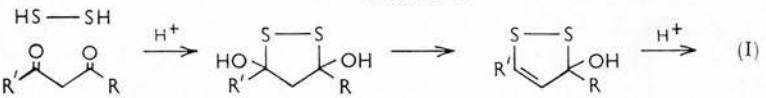


(III)

a: R = R′ = Ph; b: R = Me, R′ = Ph;
c: R = Ph, R′ = Me; d: R = CH_2Ph, R′ = Ph
e: R = R′ = H; f: R = H, R′ = Ph
g: R = *p*-$Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH$, R′ = Ph

The observation by Bloch and his co-workers [3] that hydrogen disulphide adds readily to the carbonyl group of aromatic aldehydes suggested that reaction of the disulphide with β-diketones might afford a route to 1,2-dithiolium salts according to Scheme 1.

Scheme 1.



Accordingly, dibenzoylmethane, benzoylacetone, and acetylacetone were allowed to react with hydrogen disulphide in benzene saturated with hydrogen chloride. The first two compounds yielded crystalline chlorides which were converted into the more stable perchlorates (Ia and b; X = ClO_4); benzoylacetone reacted the more rapidly and gave the better yield. Acetylacetone, however, gave only a syrup which, although insoluble in benzene, showed no salt-like properties and did not yield a perchlorate.

Consideration of the methods employed for synthesis of azoles and of thiopyrylium salts [4] led us to suppose that 1,3-dithiolium salts might be formed by acid-catalysed cyclisation of α-oxoalkyl dithiocarboxylates, R·CO·CH_2·S·CS·R′. Phenacyl dithiobenzoate gave a 40% yield of the chloride (IIa) during three weeks in ether saturated with hydrogen chloride, but when the solution was also saturated with hydrogen sulphide (method A), a better yield (98%) was obtained in a shorter time (4 days). α-Phenylphenacyl dithiobenzoate did not cyclise in ether but, with hydrogen sulphide and perchloric acid in boiling acetic acid (method B), it afforded a good yield of triphenyl-1,3-dithiolium perchlorate. Acetonyl dithiobenzoate and phenacyl dithioacetate and phenyl(dithioacetate) yielded dithiolium salts by method A. The last two compounds gave a better yield when boron trifluoride was used instead of hydrogen chloride, but the effect of boron trifluoride on the yields of other dithiolium salts was not investigated. The cation (perchlorate salt), and its conjugate base, obtained from phenacyl phenyl(dithioacetate) corresponded in melting